Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supporting Information (ESI)

Harnessing Solution and Solid-state Emissive Materials from Aliphatic Biogenic Amine-induced Transient Assembly and Spontaneous Disassembly†

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General Information

A. Materials and methods:

The chemicals $AlCl_3$, Bromine and Copper cyanide (CuCN) were purchased from Spectrochem and used as received. Pyrene and 2-chloro-2-methylropane (*tert*-butyl chloride) were bought from Alfa-Aesar and Sigma-Aldrich respectively. 1,3-dimethyl-2-imidazolidinone (DMI) was purchased from TCI chemicals, Acetic acid and acetic anhydride were bought from Merck and Pallav chemicals. Ethylene diamine, 1,3-diaminopropane and triethylamine (TEA) were purchased from Spectrochem. 1,5-diaminopentane, 1,6-diaminohexane and spermidine were procured from Alfa-Aesar and 1,4-diaminobutane, spermine were purchased from Sigma-Aldrich. *N, N*-dimethylamino propylamine was bought from Fluka Chemical. The polymer polymethyl methacrylate (PMMA) was bought from Sigma-Aldrich and used as received. The reference dye coumarin-153 and Quinine sulfate were purchased from Sigma-Aldrich and used as received. The spectroscopic grade solvents such as toluene, DCM, THF, EtOAc, ACN, MeOH and DMSO were purchased from Sisco Research Laboratories (SRL) and used for spectroscopic measurements after received. For the spectroscopic measurement, K_2CO_3 treated $CHCl_3$ was properly dried to remove the acid impurity and used as obtained. The NMR solvents $CDCl_3$ and D_2O were purchased from Sigma Aldrich. The quartz plate used for solid-state photophysical measurements was purchased from Techinstro. Before using, the quartz plate was properly cleaned in presence of dilute acid solution followed by Milli-Q water, acetone and ethanol. To purify the compounds, Silica gel (100-200 mesh) from Merck was used for column chromatography.

B. Instrumentation details:

1. NMR spectroscopy and mass spectrometry:

^1H NMR spectra were recorded using Bruker-500 MHz spectrometer. For ^{13}C NMR, frequency was kept as 126 MHz. The chemical shifts of the compounds were calculated with respect to residual solvent peak of $CDCl_3$ (δ = 7.26 ppm) and the coupling constant J-value was determined in Hz unit. The Atmospheric Pressure Chemical Ionization (APCI) mass spectrometry data were recorded using Bruker Micro-TOF-Q-II mass spectrometer and $CHCl_3$ was used as eluent.

2. Steady-state absorption and fluorescence measurements:

Steady-state absorption spectra in solution were recorded using Shimazu 1800 UV-Vis. spectrophotometers using quartz cuvette of 1 cm path length. Steady-state fluorescence spectra were measured by HORIBA Jobin Yvon Fluorolog using the same quartz cuvette of 1 cm path length. For the photophysical measurements, the stock concentration of **Py-DA** and biogenic amines were maintained as 1.0 mM and 10 mM in $CHCl_3$ respectively. During the fluorescence measurement, both excitation and emission slits were kept as 1.5/ 1.5 nm. For the solid-state measurement, the solution was drop-casted on a quartz plate and the plate was placed in the solid-state holder at a magic angle. Temperature-dependent emission study were carried out using an external T-app installed in the Fluorolog instrument. For the concentration-dependent studies, the BAs were added in **Py-DA** solution and spectra were recorded instantly after addition.

3. Time-resolved fluorescence measurement:

Time-resolved fluorescence measurement or fluorescence lifetime measurement was performed using time-correlated single-photon counting (TCSPC) set up from Hamamatsu MCP Photomultiplier (R-3809U-50). For the excitation of the molecules, 373 nm and 468 nm lasers were used as excitation sources while keeping the photon count up to 10,000. The instrument response function (IRF) was determined using a dilute solution of colloidal silica named as Ludox before collecting the decay of samples. The excitation and emission polarizer were kept vertically and at a magic angle (54.55 ^{o}) respectively. The decay curve was properly fitted using the deconvolution method by EZtime software while keeping the fitting parameter χ^2 value in the range of 0.9-1.2. The lifetime was measured at room temperature (295 K) as otherwise mentioned. The excited state average lifetime was determined using the following equation:

$$\tau_{avg} = \Sigma a_i \tau_i^2 \Big/ \Sigma a_i \tau_i \quad \text{.....equation (1)}$$

where a_i denotes the contribution of i^{th} component and τ_i indicates lifetime value of i^{th} component.

4. Fluorescence quantum yield measurement:

Relative fluorescence quantum yield was measured in solution by taking Coumarine-153 (QY = 0.54 in EtOH) and Quinine sulphate in 0.5 M H_2SO_4 (QY = 0.54) as the reference dyes.[1-2]

5. Infrared Spectroscopy:

IR spectra in solution was recorded by drop-casting the **Py-DA** and Py-BA in $CHCl_3$ solution on sensor plate using Perkin-Elmer model UATR spectrum instrument.

6. Calculation of CIE chromaticity Index.[3]

The CIE chromaticity Index values were calculated by using the following equations:

$$X = \Sigma_{K=1} \Phi_K(\lambda) B_K(\lambda) \text{……..equation (2)}$$

$$Y = \Sigma_{K=1} \Phi_K(\lambda) G_K(\lambda) \text{…….equation (3)}$$

$$Z = \Sigma_{K=1} \Phi_K(\lambda) R_K(\lambda) \text{……..equation (4)}$$

Where the Tristimulus values X, Y, Z represent a specific color in color coordinates. $B_K(\lambda)$, $G_K(\lambda)$, $R_K(\lambda)$ are defined as color matching functions of a standard colorimetric observer. $\Phi_K(\lambda)$, spectral distribution of color stimulus obtained from the emission spectra of species. The CIE co-ordinates (x, y, z) were calculated by considering the equations: x = X/(X+Y+Z), y = Y/(X+Y+Z) and z = Z/(X+Y+Z).

7. Thin film preparation:

For preparing the desired solution, **Py-DA** (Stock concentration: 10 mM) was dissolved in dry $CHCl_3$, then 1,4-DAB or Spermidine was added to make it final concentration as 20 mM. After 10 mins of addition of BA, the solution became blue emissive. Then, thin films were prepared by simple drop-casting of Py-BA solution on a cleaned quartz plate and dried properly by keeping it in hot air oven for 2 h at 100 °C. With the properly dried film, the absorption and consequently emission spectra were measured using the front-face excitation method.

8. Theoretical investigations:

To investigate the aggregation behavior of the pyrene dianhydride (**Py-DA**) and the influence of Biogenic amines (BAs) on the aggregation pattern, we have performed theoretical calculations on the modelled dimeric species in gas phase by using density functional theory (DFT) at Gaussian-16 programme.[4] As dispersion effects seem to have a significant role in the aggregation pattern, we have employed dispersion corrected hybrid functional (B3LYP-D3) and suitable basis sets, 6-311G (d, p) for all the atoms. In order to compute the absorption properties of the composite systems, we have used log-range corrected functional, CAM-B3LYP with the similar basis sets as mentioned earlier. All the separate molecules and the composite systems were allowed to relax to get the optimized ground state geometries. The optimized geometries were then treated with time-dependent DFT (TDDFT) calculations

which simulate absorption properties of the species. For that simulation, we adopted polarizable continuum model, using the integral equation formalism variant (IEFPCM) in chloroform solvent. The transition characteristics were determined by analyzing the molecular orbitals involved in it.

9. Field emission scanning electron microscopy (FESEM) study:

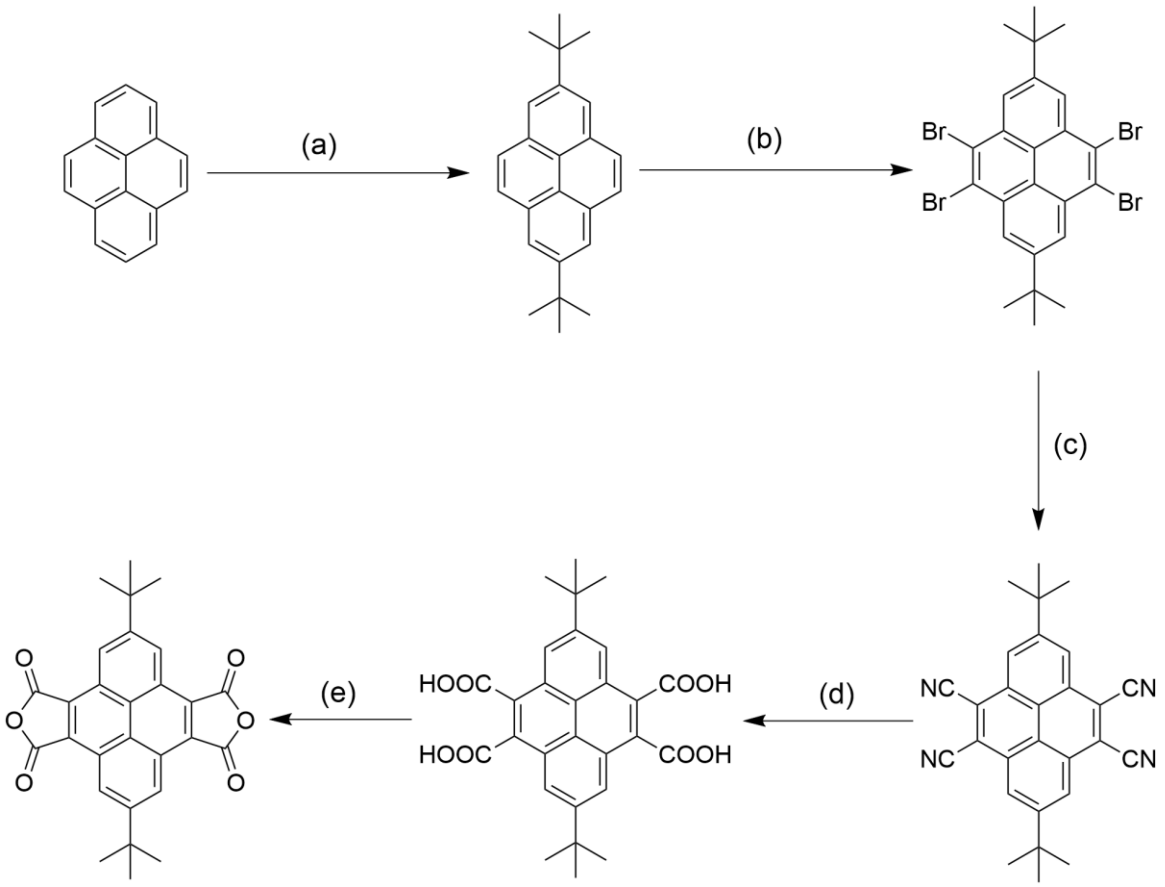
For the FESEM investigation, the solution was drop-casted on a properly cleaned cover-slip kept on a black carbon tape coated stub. The sample was properly dried under high vacuum for overnight prior to collection of images. The images were collected using High resolution FESEM from Zeiss, model – ULTRA Plus. The voltage was kept as low as 20 kV.

10. Cell culture and live-cell imaging experiments:

BHK-21 cells were purchased from NCCS, Pune (India). Dulbecco's Modified Eagle Medium (DMEM), Fetal Bovine Serum (FBS), and L-Glutamine-Penicillin-Streptomycin Solution (antibiotic cocktail) were purchased from HiMedia (USA). Lipopolysaccharides (from *Escherichia coli*) were purchased from Sigma Aldrich (USA). The glass bottom imaging dishes were purchased from Ibidi (Germany). The cells were cultured in DMEM + 10% FBS + 1% antibiotic cocktail in the CO_2 incubator at 37 ^{o}C and 70 – 80% confluency were taken to prepare imaging dishes. After incubation with the molecule of interest, cells were washed with PBS before confocal imaging.

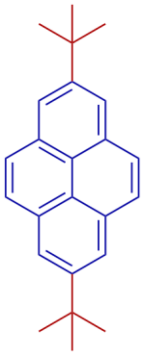
All the confocal imaging experiments were performed using the Olympus FLUOVIEW 3000 microscope with live-cell imaging set up. The image processing was done with the help of cellSens Dimension software (Olympus). For fluorescence imaging, 405/488 nm (probe of interest) and 561 nm (LysoTracker green, MitoTracker green, ER-Tracker green) excitation lasers were used. The confocal aperture was kept at 1.0 Airy Disk (AU) while the dwell time is 4 μs/pixel. The images were acquired in sequential scan mode which ensures that the two fluorophores are not excited simultaneously.

C. Synthetic procedures:



(a) Anhydrous $AlCl_3$, DCM, *tert*-butyl chloride, RT, 24 h, 80% (b) Br_2, CCl_4, Fe powder, RT, 4 h, 90% (c) CuCN, DMI, excess Mohr's salt, reflux, 2.5 h, 30% (d) KOH, EtOH/ H_2O, reflux, 48 h, 81% (e) Acetic acid/ acetic anhydride, reflux, 18 h, 64%.

Scheme S1. Synthetic routes of Pyrene-dianhydride (**Py-DA**).

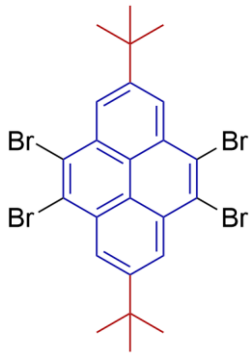


Synthesis of 2,7-di-*tert*-butylpyrene: Pyrene (1 g, 4.94 mmol), and $AlCl_3$ (266 mg, 1.99 mmol) were taken in a 100 mL RB flask and dissolved with 50 mL anhydrous DCM. *Tert*-butyl chloride (3 mL, 27.22 mmol) was slowly added to the above solution under N_2 atmosphere. The reaction mixture was

stirred for 24 h at room temperature. After completion of the reaction, the compound was extracted using DCM-H_2O mixture, Solvent was evaporated under reduced pressure and the crude was purified by column chromatography using distilled $CHCl_3$ as an eluent. Finally, the desired compound was obtained as pure after doing precipitation using MeOH/ $CHCl_3$ mixture. The title compound was obtained as 1.24 g; yield – 80%.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.18 (s, 4H), 8.02 (s, 4H), 1.58 (s, 18H)

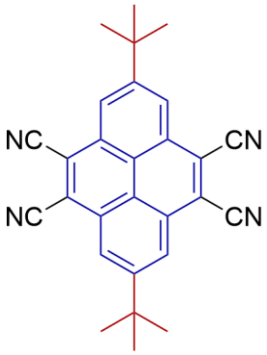
^{13}C NMR (126 MHz, Chloroform-*d*): δ 32.2, 35.4, 122.2, 123.1, 127.6, 131.0, 148.8.



Synthesis of 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene: In a 250 mL RB flask, 2,7-di-tert-butyl-pyrene (500 mg, 1.59 mmol) was dissolved in 30 mL carbon tetrachloride (CCl_4). In another vial, Br_2 (0.5 mL, 9.76 mmol) was dissolved in 10 mL CCl_4 to get a mixture. Then, Fe powder (161 mg, 2.883 mmol) was added in CCl_4 dissolved 2,7-*tert*-butylpyrene solution and consequently, the mixture of Br_2 in CCl_4 was dropwise added in the resulting solution. The reaction was stirred at RT for 4 h. After the reaction was completed, the solvent was evaporated under reduced pressure and crude was purified by column chromatography in DCM. The title compound was obtained as pure white solid (900 mg, Yield- 90%).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.87 (s, 4H), 1.62 (s, 18H)

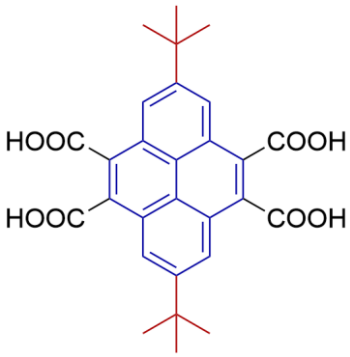
^{13}C NMR (126 MHz, Chloroform-*d*): δ 32.1, 36.0, 122.1, 126.3, 127.1, 130.3, 151.4.



Synthesis of 2,7-di-*tert*-butyl-4,5,9,10-tetracyanopyrene: In a 100 mL RB flask, 2,7-di-tert-butyl-4,5,9,10-tetrabromopyrene (1.1 g, 1.17 mmol) and CuCN (1.5 g, 17 mmol) were mixed properly. Consequently, 50 mL 1,3-dimethyl-2-imidazolidinone (DMI) solvent was added to the mixture. The resulting mixture was stirred at 250 ˚C for 2.5 h. After removal of solvent, the solution was cooled down to 80 ˚C and a large amount of Mohr's salt in water was added to the mixture. The mixture was stirred for 2 h. The mixture was filtered and washed with H_2O and DCM. The solid mixture was collected and DCM was removed. The crude product was purified by performing column chromatography using DCM-Hexane solvent mixture at 4:1 ratio as an eluent. The desired compound was afforded as yellow solid, Yield – 30%.

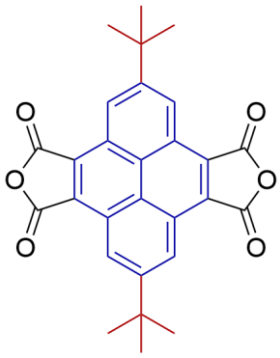
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.93 (s, 4H), 1.66 (s, 18H)

^{13}C NMR (126 MHz, Chloroform-*d*): δ 31.9, 36.4, 114.5, 118.3, 123.2, 126.9, 126.9, 154.4.



Synthesis of 2,7-di-*tert*-butyl-4,5,9,10-pyrenetetracarboxylic acid: 2,7-di-*tert*-butyl-4,5,9,10-tetracyanopyrene (195 mg, 0.397 mmol) and KOH (1.1 g, 19.60 mmol) were taken in a 50 mL RB flask. The mixture was dissolved in a solvent mixture of EtOH/H_2O (1:1 ratio, 8 mL) and was stirred at reflux condition for 48 h. After cooled down to RT, the solution was filtered by funnel and HCl was dropwise added to acidify the filtrate. A yellow-colored precipitate appeared in the solution which was collected by filtration. The compound was afforded as bright-yellow solid (186 mg). As, it was poorly

soluble in common organic solvents such as $CHCl_3$, DCM, EtOAc and hexane, we could not perform the column chromatography for this compound. Therefore, the compound was used for the next step reaction without any further purification, Yield – 81%.

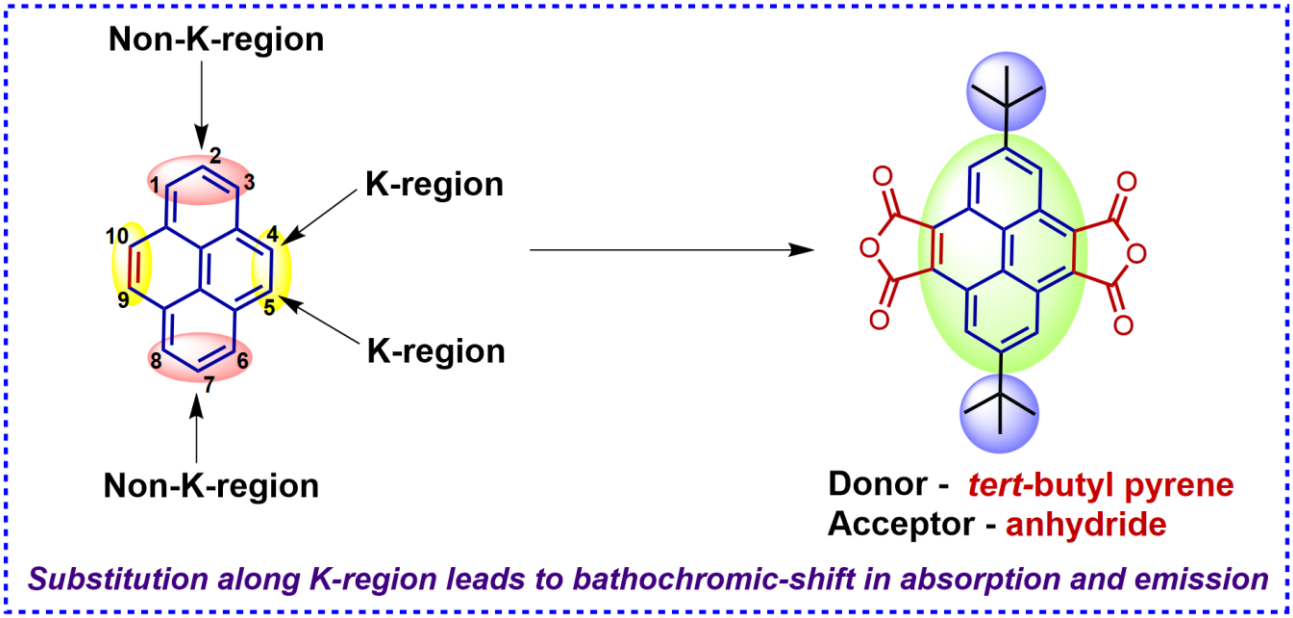


Synthesis of 2,7-di-*tert*-butyl-4,5,9,10-pyrenetetracarboxylic dianhydride: 2,7-ditertbutyl-4,5,9,10-pyrenetetracarboxylic acid was taken in an RB and dissolved in acetic acid/ acetic anhydride solvent (volume ratio 1:1, 9 mL). The mixture was heated to reflux and kept for overnight stirring. After cooling to RT, H_2O was added and the precipitate was collected after proper washing with H_2O. The purification of the compound was done by column chromatography using $CHCl_3$ as an eluent which afforded the title compound as light-yellow solid, Yield – 64%.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 9.57 (s, 4H), 1.67 (18 H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 31.9, 36.4, 124.2, 126.1, 128.6, 130.0, 154.2, 163.4.

D. Spectroscopic investigations:



Scheme S2. Representation of K-regions and non-K-regions in pyrene and influence of substitutions on tuning of its photophysical properties.

Absorption, emission and fluorescence lifetime studies of Py-DA in different solvents

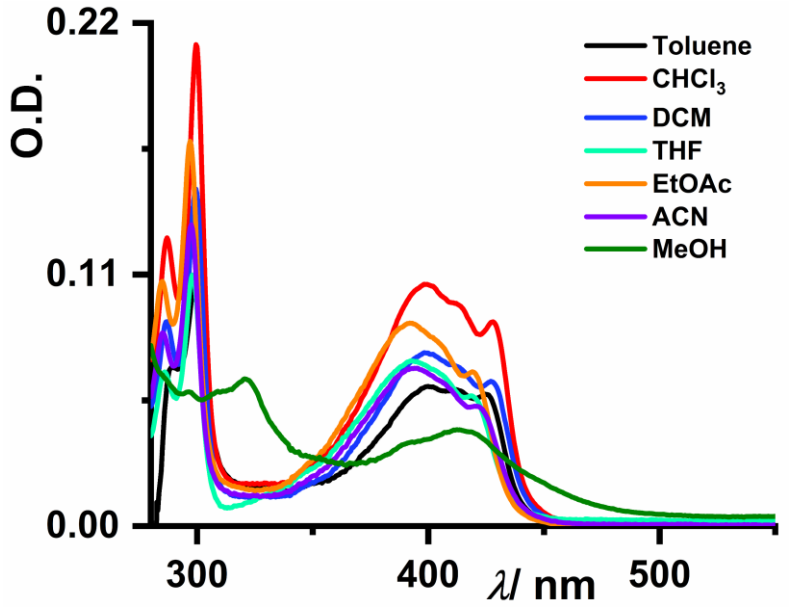


Fig. S1 Absorption spectra of **Py-DA** (5 μM) in different solvents with varying polarity.

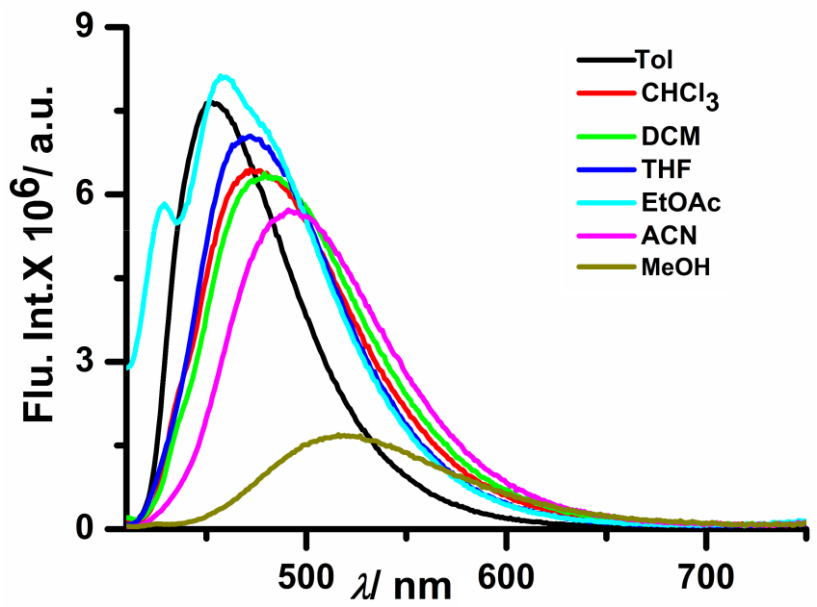


Fig. S2 Emission spectra of **Py-DA** (5 μM) in different solvents with varying polarity.

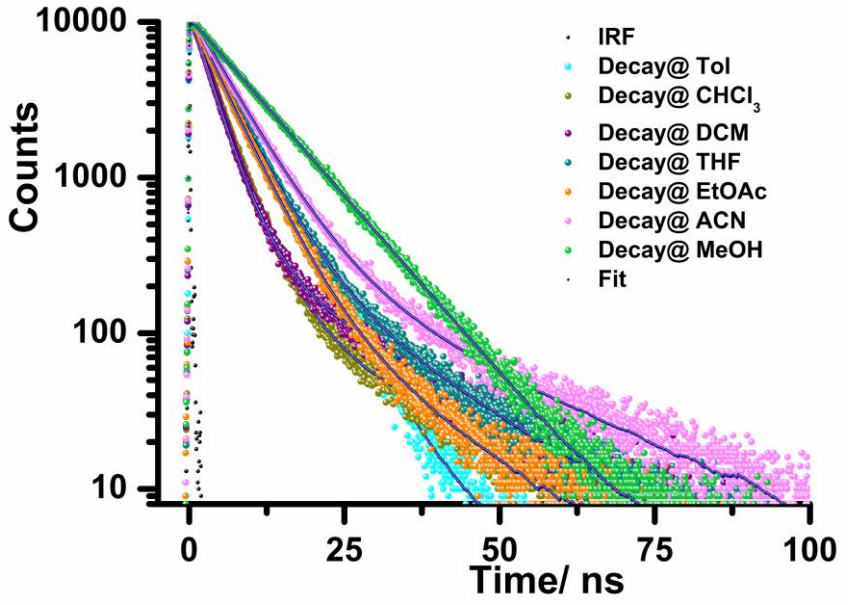


Fig. S3 Solvent-dependent fluorescence lifetime decay of **Py-DA** (5 μM) in different non-polar to polar solvents; lifetime decays were monitored at their respective emission maxima in solvents, λ_{ex}= 468 nm.

Table S1. Photophysical results of **Py-DA** (5 μM) in various solvents

Solvents	λ_{max}^{abs}/ **nm**	λ_{max}^{em}/ **nm**	**Stokes shift/ nm**	**Rel.** Φ_{Fl}[a] **(%)**	τ_{avg}/ **ns**
Toluene	400	453	53	34.2	5.9
$CHCl_3$	400	470	70	22.7	8.8
DCM	398	480	82	30.2	11.2
THF	392	472	80	29.8	9.6
EtOAc	392	458	66	22.8	7.4
ACN	393	492	99	26.0	5.8
MeOH	414	518	104	6.4	9.5

Note: [a] Rel. Φ_{Fl} values were calculated w.r.t Coumarin 153 as reference dye (Φ_{Fl} = 54.4% in ethanol).[2]

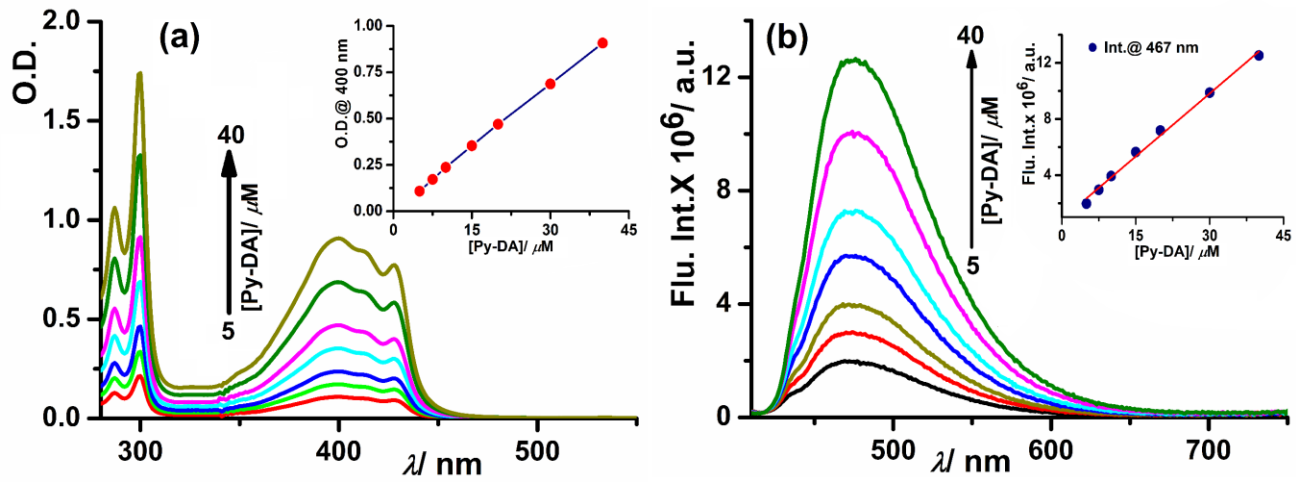


Fig. S4 (a) Concentration-dependent (a) absorption (5 μM) (b) emission spectra of **Py-DA** in $CHCl_3$, insets showing a linear dependence of O.D. and intensity with concentration. $\lambda_{ex.}$ = 400 nm for emission measurement.

Absorption study of Py-DA with different BAs:

Py-DA with EDA:

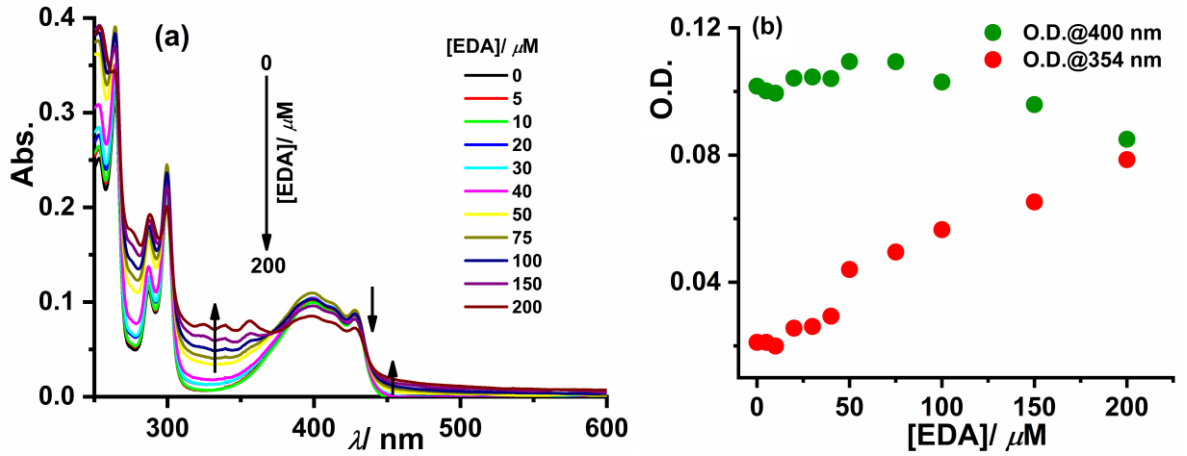


Fig. S5 (a) UV-Vis. spectra of **Py-DA** (5 μM) with EDA (0-200 μM) in $CHCl_3$, (b) representation of change in O.D. at 400 nm and 354 nm with concentration of EDA in $CHCl_3$.

Py-DA with 1,3-DAP:

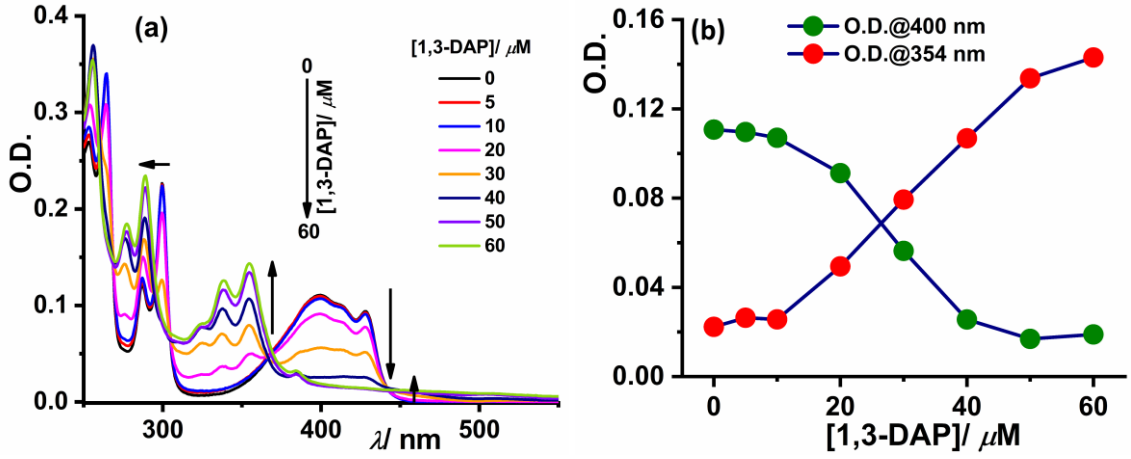


Fig. S6 (a) UV-Vis. spectra of **Py-DA** (5 μM) with 1,3-DAP (0-60 μM) in $CHCl_3$, (b) representation of change in O.D. at 400 nm and 354 nm with conc. of 1,3-DAP in $CHCl_3$.

Py-DA with N, N-DMPA:

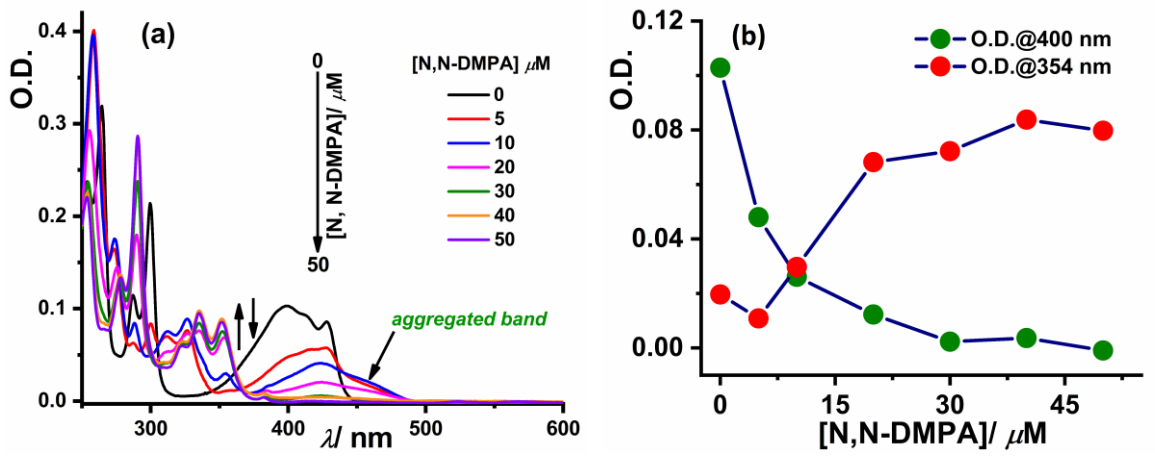


Fig. S7 (a) UV-Vis. spectra of **Py-DA** (5 μM) with *N*, *N*-DMPA (0-50 μM) in $CHCl_3$, (b) representation of change of O.D. at 400 nm and 354 nm with conc. of *N*, *N*-DMPA in $CHCl_3$.

Py-DA with 1,5-DAP:

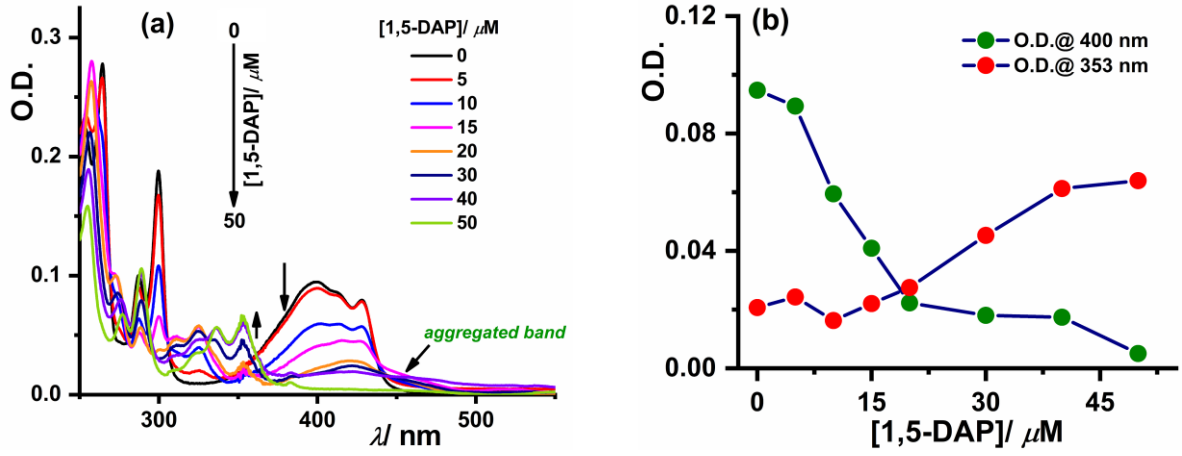


Fig. S8 (a) UV-Vis. spectra of **Py-DA** (5 μM) with 1,5-DAP (0-50 μM) in $CHCl_3$, (b) representation of change of O.D. at 400 nm and 353 nm with conc. of 1,5-DAP in $CHCl_3$.

Py-DA with 1,6-DAH:

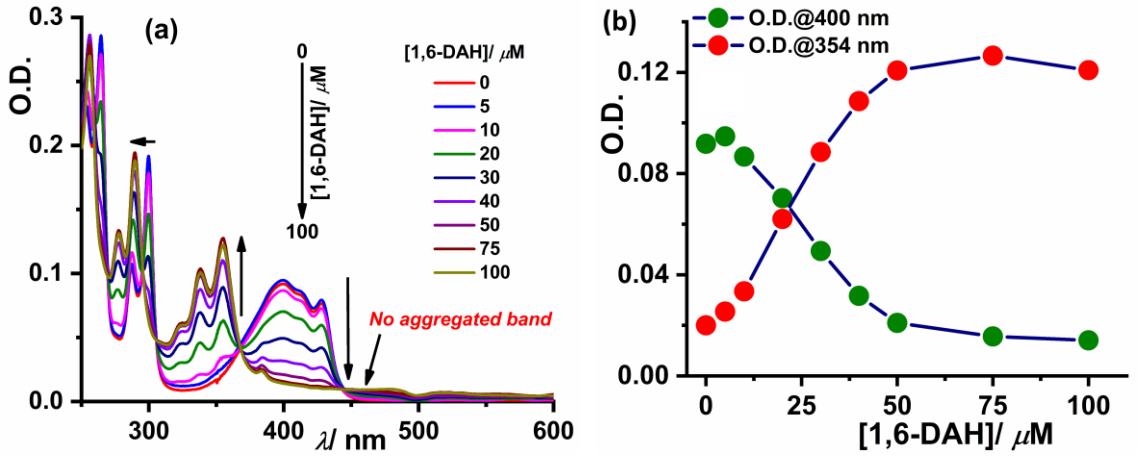


Fig. S9 (a) UV-Vis. spectra of **Py-DA** (5 μM) with 1,6-DAH (0-100 μM) in $CHCl_3$, (b) representation of change of O.D. at 400 nm and 354 nm with conc. of 1,6-DAH in $CHCl_3$.

Py-DA with spermidine:

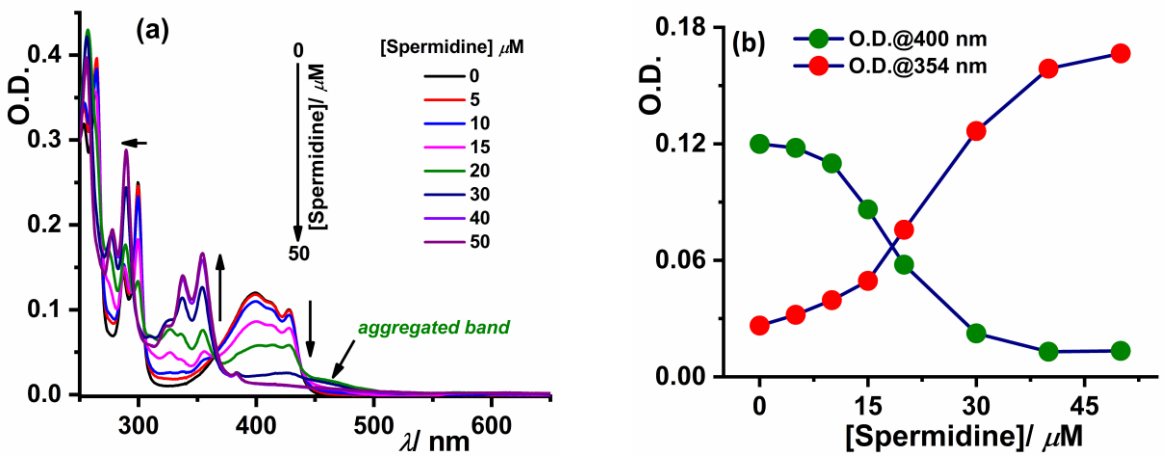


Fig. S10 (a) UV-Vis. spectra of **Py-DA** (5 μM) with spermidine (0-50 μM) in $CHCl_3$, (b) representation of change of O.D. at 400 nm and 354 nm with conc. of spermidine in $CHCl_3$.

Note: *Here we presume, the small hump appeared at 384 nm is attributed to S_0-S_1 transition and absorption peaks nearby 355 nm and 335 nm are the 0-0 and 0-1 vibronic bands in S_0-S_2 transition and consequently, the structured band below 300 nm is a result of S_0-S_3 transition, as described in literature.*[5]

Table S2. Summary of $A_{0\text{-}0}$/ $A_{0\text{-}1}$ ratio with concentration for different BAs

	$A_{0\text{-}0}$ (355 nm)/ $A_{0\text{-}1}$ (337 nm) for Py-BAs					
BAs conc./ μM	**1,3-DAP**	**1,4-DAB**	**1,5-DAP**	**1,6-DAH**	**Spermidine**	**Spermine**
5	_[a]	_[a]	_[a]	_[a]	_[a]	1.01
10	_[a]	_[a]	_[a]	1.65	1.45	1.00
20	1.36	1.00	0.92	1.38	1.06	0.98
30	1.12	1.00	1.02	1.29	1.10	0.99
40	1.10	1.01	1.10	1.26	1.17	_[b]
50	1.15	1.00	1.13	1.25	1.19	_[b]

Note: *$A_{0\text{-}0}$ and $A_{0\text{-}1}$ are the absorbance corresponding to 0-0 and 0-1 transitions of Py-BA conjugates monitored at 355 nm and 337 nm respectively. $A_{0\text{-}0}$ and $A_{0\text{-}1}$ are considered to those concentrations where the spectra showed the appearance of two transitions. [a]no appearance of the peak, hence values are not given. [b]For **Py-Spermine** conjugate, the absorption spectra did not exhibit any further change at 30 μM, therefore higher concentrations have not been considered here. $A_{0\text{-}0}$/ $A_{0\text{-}1}$ ratio obtained closer to 1.0 denotes the formation of H-type pre-associated dimer in the ground state.*

Emission study of Py-DA with different BAs:

Py-DA with EDA:

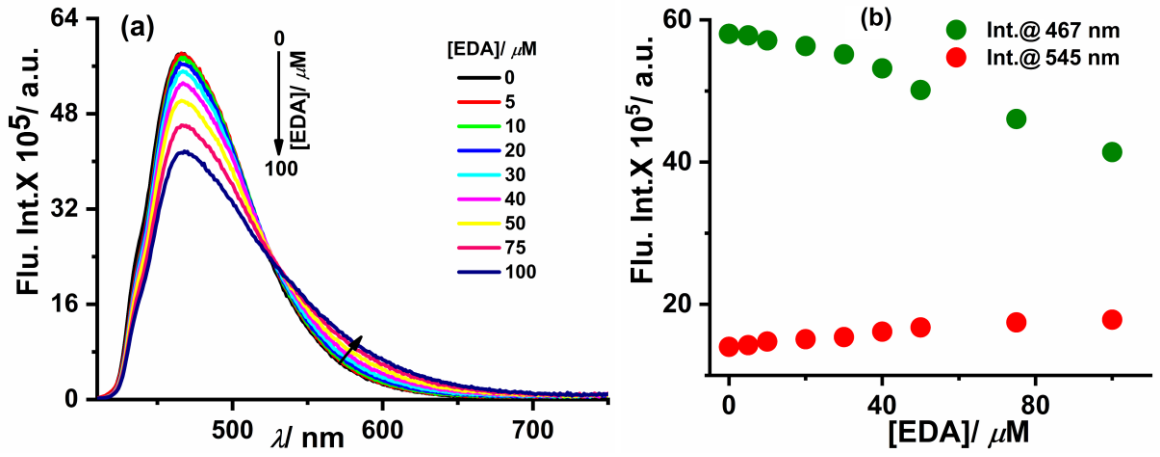


Fig. S11 (a) Fluorescence spectra of **Py-DA** (5 μM) with EDA (0-100 μM) in $CHCl_3$, (b) representation of change of intensity at 467 nm and 545 nm with conc. of EDA in $CHCl_3$.

Py-DA with 1,3-DAP:

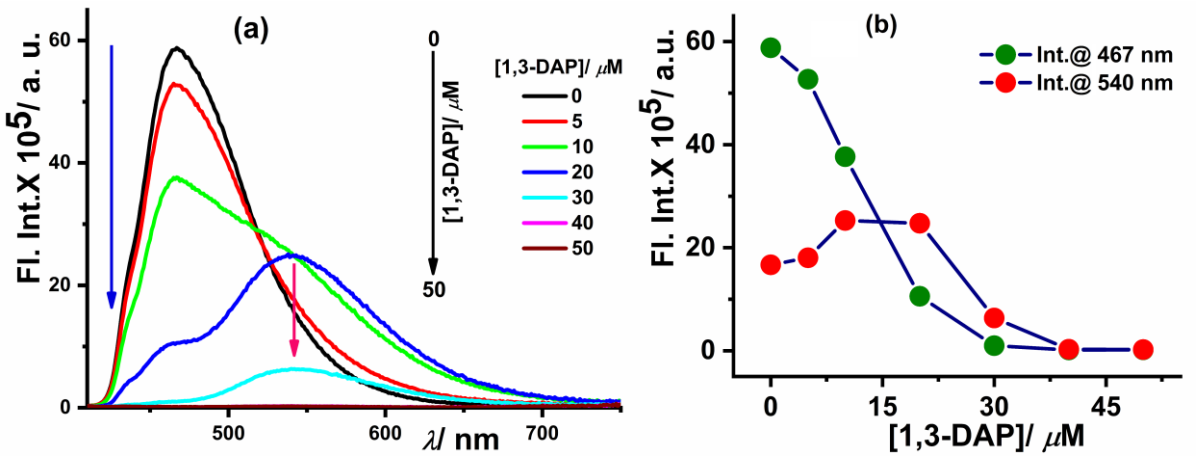


Fig. S12 (a) Fluorescence spectra of **Py-DA** (5 μM) with 1,3-DAP (0-50 μM) in $CHCl_3$, (b) representation of change of intensity at 467 nm and 540 nm with conc. of 1,3-DAP in $CHCl_3$.

Py-DA with N, N-DMPA:

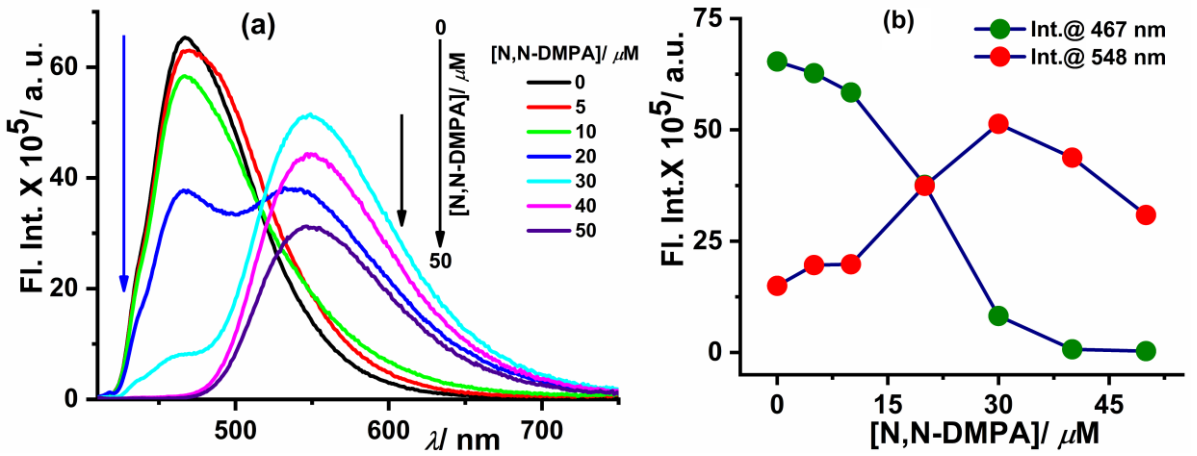


Fig. S13 (a) Fluorescence spectra of **Py-DA** (5 μM) with *N*, *N*-DMPA (0-50 μM) in $CHCl_3$ (b) representation of change of intensity at 467 nm and 548 nm with conc. of *N*, *N*-DMPA in $CHCl_3$.

Py-DA with 1,5-DAP:

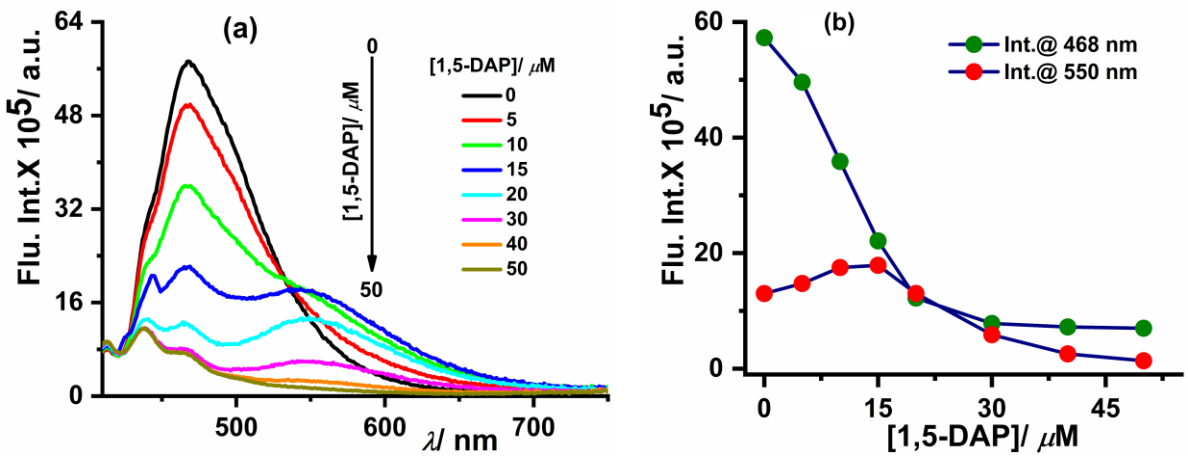


Fig. S14 (a) Fluorescence spectra of **Py-DA** (5 μM) with 1,5-DAP (0-50 μM) in $CHCl_3$ (b) representation of change of intensity at 468 nm and 550 nm with conc. of 1,5-DAP in $CHCl_3$.

Py-DA with 1,6-DAH:

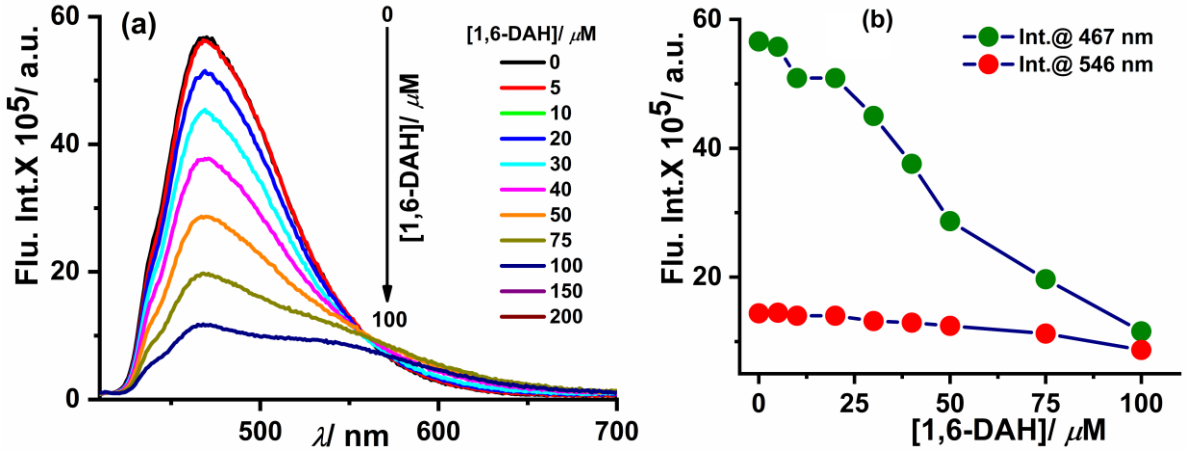


Fig. S15 (a) Fluorescence spectra of **Py-DA** (5 μM) with 1,6-DAH (0-100 μM) in $CHCl_3$ (b) representation of change of intensity at 467 nm and 546 nm with conc. of 1,6-DAH in $CHCl_3$.

Py-DA with Spermidine:

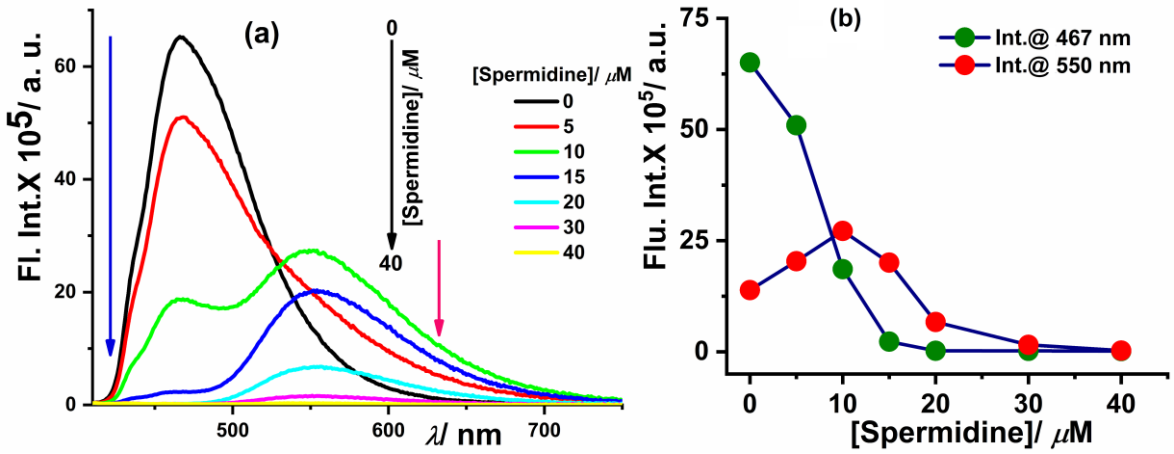


Fig. S16 (a) Fluorescence spectra of **Py-DA** (5 μM) with spermidine (0-40 μM) in $CHCl_3$ (b) representation of change of intensity at 467 nm and 550 nm with conc. of spermidine in $CHCl_3$.

Graphical representation of band intensity ratio *vs* concentration for BAs:

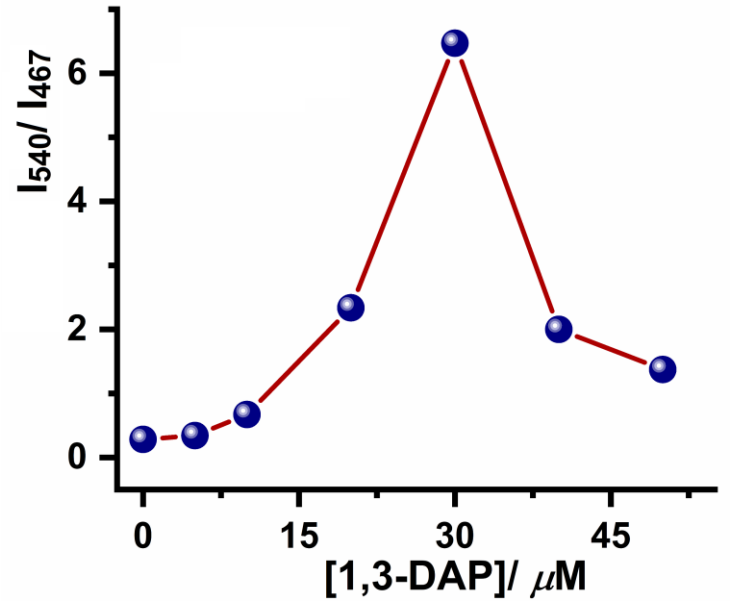


Fig. S17 Representation of change of I_{540}/I_{467} ratio with concentration of 1,3-DAP in $CHCl_3$. The maximum value of I_{540}/ I_{467} ratio was obtained at 30 μM concentration of 1,3-DAP. [**Py-DA**] = 5 μM. This graph was plotted from Fig. S12.

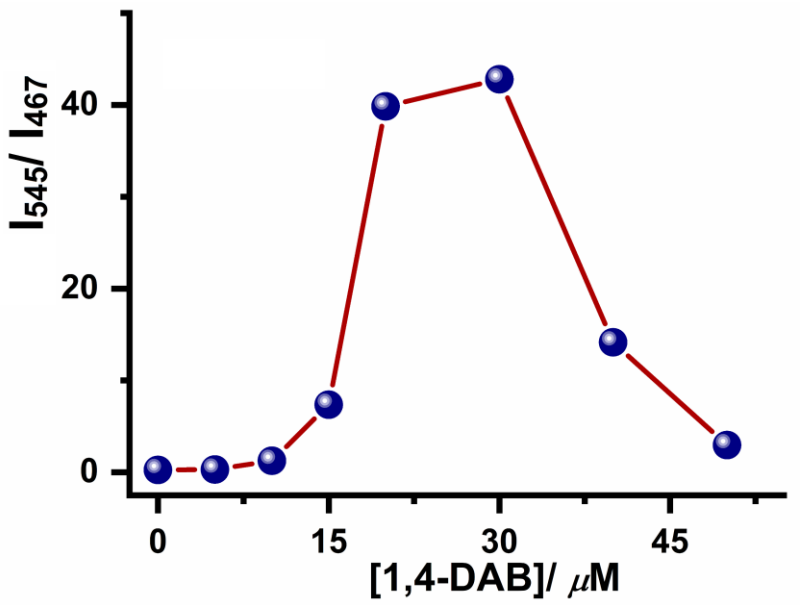


Fig. S18 Representation of change of I_{545}/I_{467} ratio with concentration of 1,4-DAB in $CHCl_3$. The maximum value of I_{545}/ I_{467} ratio was obtained at 30 μM concentration of 1,4-DAB. [**Py-DA**] = 5 μM. This graph was plotted from Fig. 1c.

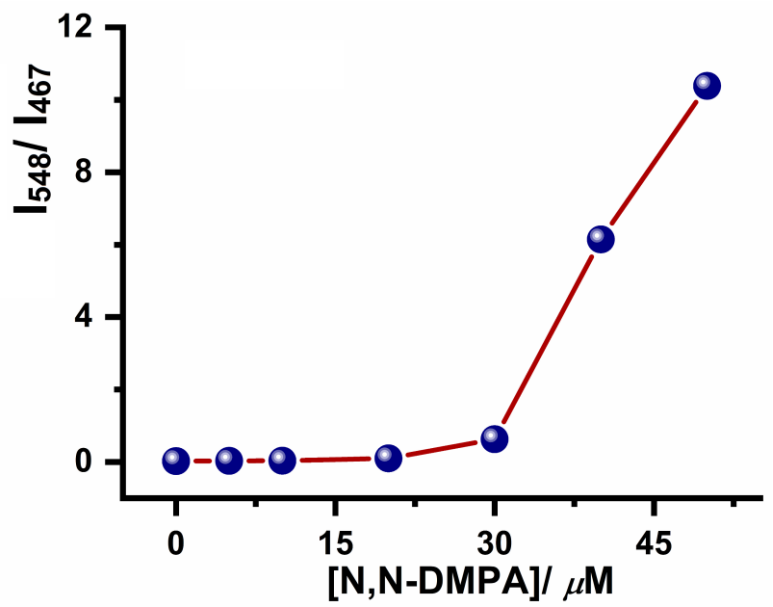


Fig. S19 Representation of change of I_{548}/I_{467} ratio with concentration of *N*, *N*-DMPA in $CHCl_3$. *N*, *N*-DMPA did not show triangular shaped plot in 0-50 μM concentration range. [**Py-DA**] = 5 μM. This graph was plotted from Fig. S13.

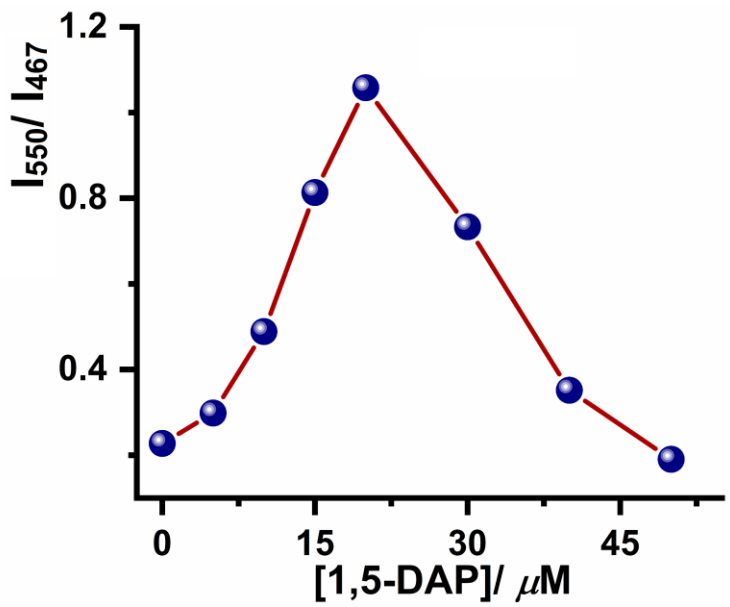


Fig. S20 Representation of change of I_{550}/I_{468} ratio with concentration of 1,5-DAP in $CHCl_3$. The maximum value of I_{550}/ I_{468} ratio was obtained at 20 μM concentration of 1,5-DAP. [**Py-DA**] = 5 μM. This graph was plotted from Fig. S14.

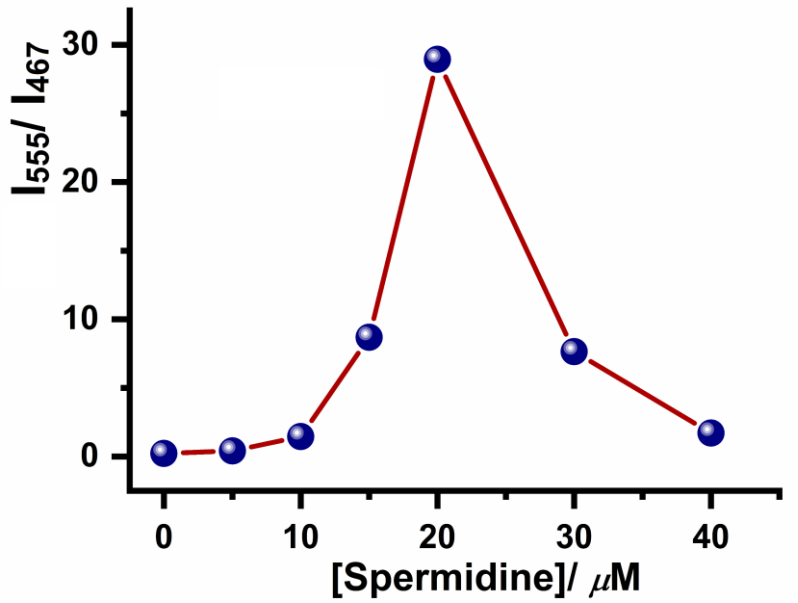


Fig. S21 Representation of change of I_{555}/I_{467} ratio with concentration of spermidine in $CHCl_3$. The maximum value of I_{555}/ I_{467} ratio was obtained at 20 μM concentration of spermidine. [**Py-DA**] = 5 μM. This graph was plotted from Fig. S16.

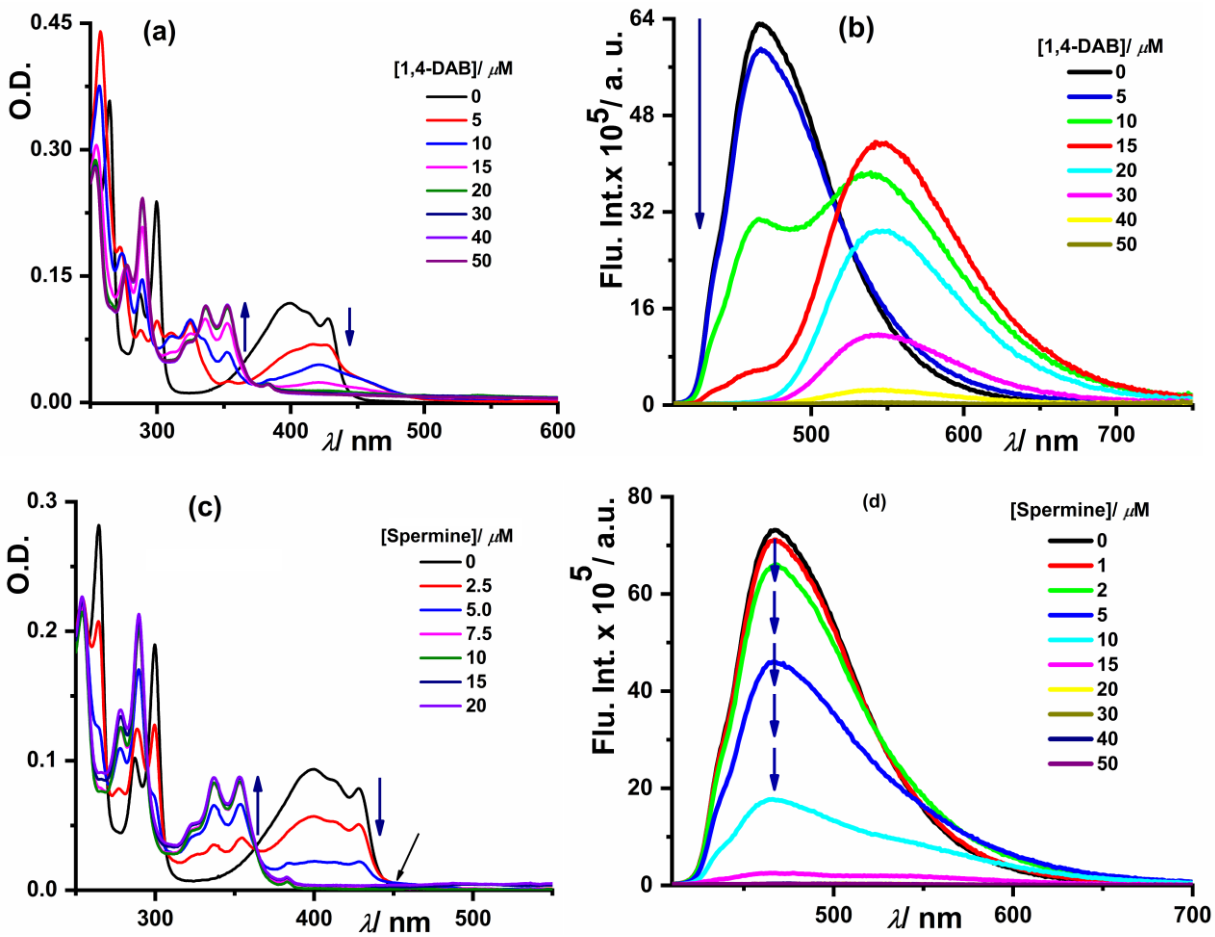


Fig. S22 Concentration-dependent (a) absorption and (b) emission spectra for **Py-DA** with 1,4-DAB in $CHCl_3$, Concentration-dependent (a) absorption and (b) emission spectra for **Py-DA** with spermine in $CHCl_3$; inset object representing the color of each spectrum inside corresponding figures.

Fluorescence lifetime decay of Py-DA in presence of BAs with varying concentration:

Py-DA with 1,4-DAB:

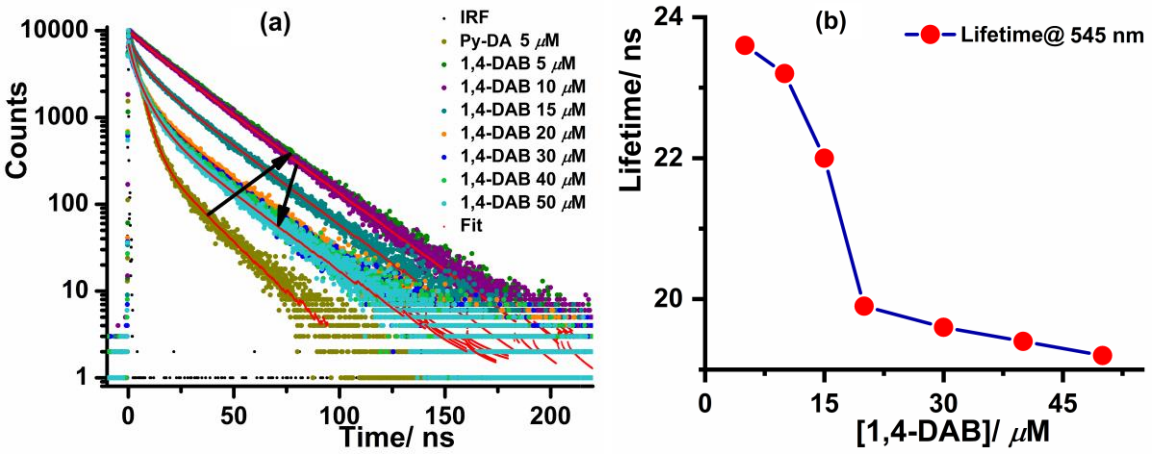


Fig. S23 (a) Fluorescence lifetime decay of **Py-DA** (5 μM) in presence of 1,4-DAB with varying concentration of 1,4-DAB in $CHCl_3$, (b) plot for change of average lifetime values with concentration, λ_{ex}= 468 nm.

Py-DA with 1,3-DAP:

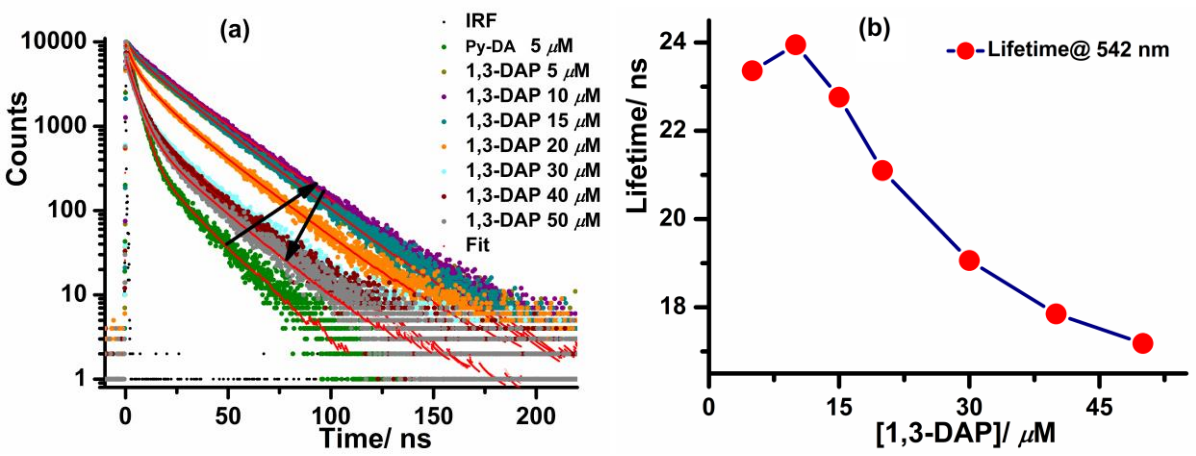


Fig. S24 (a) Fluorescence lifetime decay of **Py-DA** (5 μM) in presence of 1,3-DAP with varying concentration of 1,3-DAP in $CHCl_3$, (b) plot for change of average lifetime values with concentration, λ_{ex}= 468 nm.

Py-DA with N, N-DMPA:

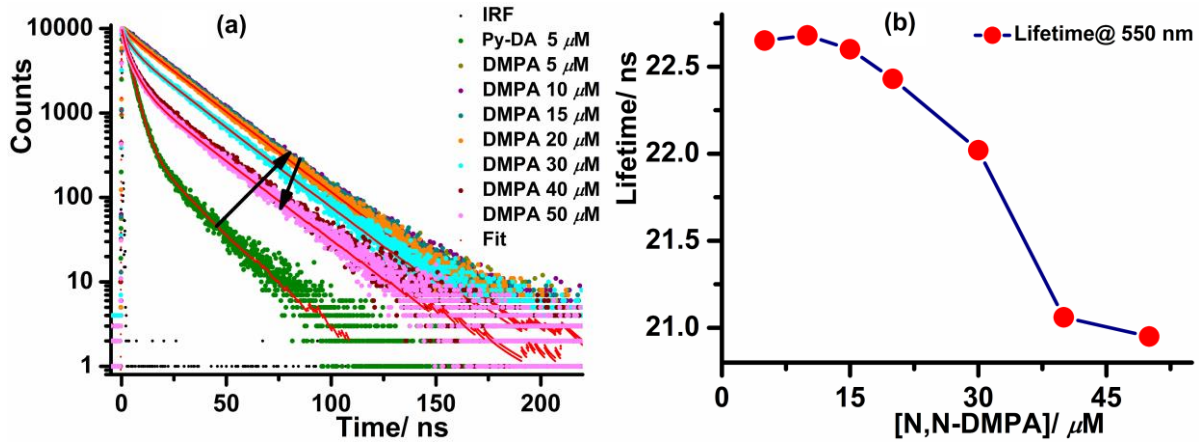


Fig. S25 (a) Fluorescence lifetime decay of **Py-DA** (5 μM) in presence of *N*, *N*-DMPA with varying concentration of *N*, *N*-DMPA in $CHCl_3$, (b) plot for change of average lifetime values with concentration, λ_{ex}= 468 nm.

Py-DA with 1,5-DAP:

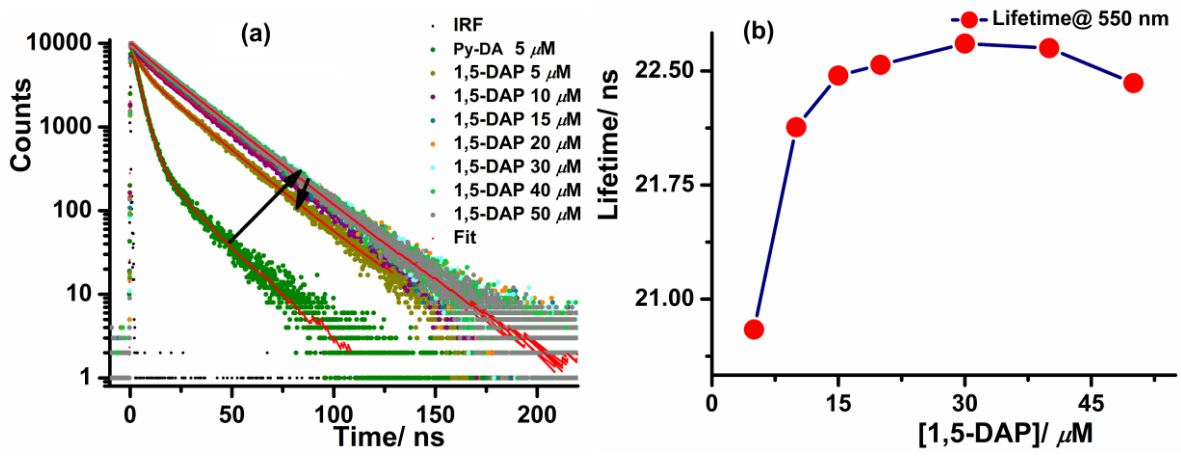


Fig. S26 Fluorescence lifetime decay of **Py-DA** (5 μM) in presence of 1,5-DAP with varying concentration of 1.5-DAP in $CHCl_3$, (b) plot for change of average lifetime values with concentration, λ_{ex}= 468 nm.

Note: *In this case, the average lifetime value did not decrease significantly even at high concentration of 1,5-DAP as observed for other Py-BAs system. This is probably due to slow dissociation of the intermediate species than other Py-BAs analogs. Hence, Fig. 26b shows a little different graph in comparison to the lifetime plots for other Py-BA systems.*

Py-DA with Spermidine:

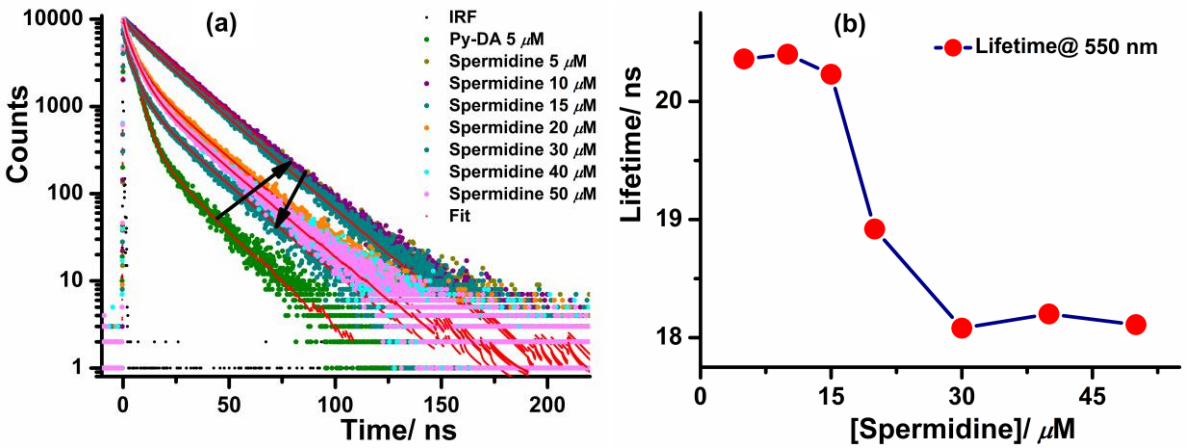


Fig. S27 Fluorescence lifetime decay of **Py-DA** (5 μM) in presence of spermidine with varying concentration of spermidine in $CHCl_3$, (b) plot for change of average lifetime values with concentration, λ_{ex}= 468 nm.

Time-dependent photophysical studies:

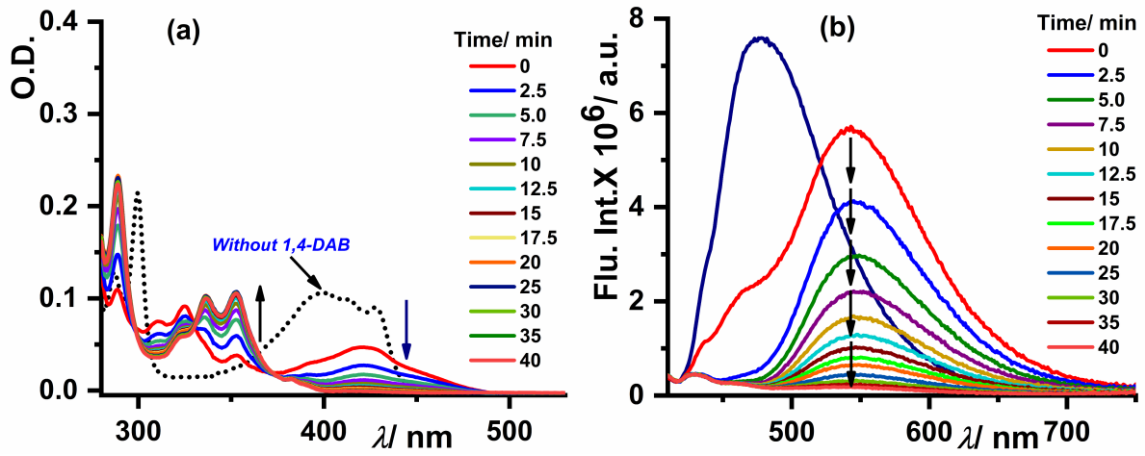


Fig. S28 Time-dependent absorption and emission spectra for **Py-DA** (5 μM) with 1,4-DAB (10 μM) in $CHCl_3$; inset object representing the color of each spectrum in the corresponding figure.

Py-DA with 1,3-DAP:

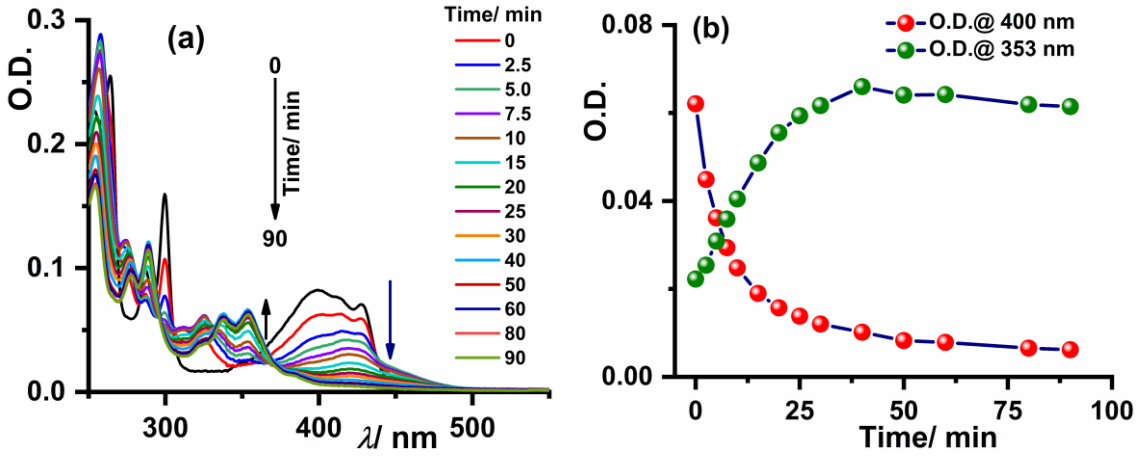


Fig. S29 (a) Time-dependent absorption spectra of **Py-DA** (5 μM) - 1,3-DAP (10 μM) showing change of absorbance, (b) representation of change of O.D. with time monitored at both 400 nm and 353 nm.

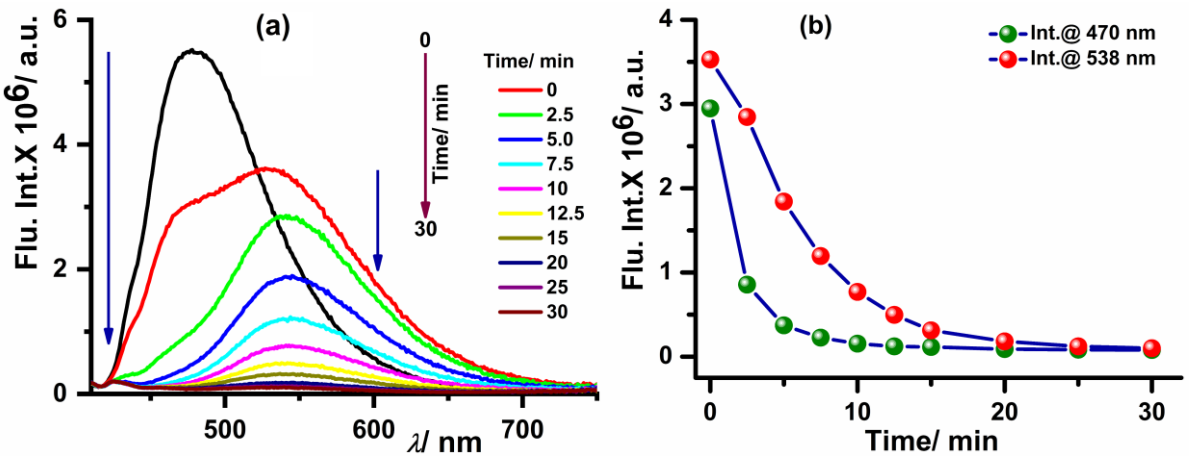


Fig. S30 (a) Time-dependent emission spectra of **Py-DA** (5 μM) - 1,3-DAP (10 μM) showing the change of emission, (b) representation of change of intensity at both 470 nm and 550 nm band with time.

Table S3. Change of $A_{0\text{-}0}$/ $A_{0\text{-}1}$ and $I_{538(TS)}$/ $I_{470\ (\mathbf{Py\text{-}DA})}$ ratio for Py-1,3-DAP conjugate with time.[a]

Time/ min	$A_{0\text{-}0}/A_{0\text{-}1}$	$I_{538(TS)}/ I_{470(Py\text{-}DA)}$
0	0.88	1.19
2.5	0.76	3.32
5.0	0.78	4.94
7.5	0.81	5.27
10.0	0.85	4.96
15.0	0.91	2.72
20.0	0.96	2.00
25.0	0.99	1.48
30.0	1.01	1.25

[a]*$A_{0\text{-}0}$ and $A_{0\text{-}1}$ are the absorbance corresponding to 353 nm and 337 nm respectively. I_{538} – intensity of transient species (TS) at 538 nm and I_{470} – intensity of* ***Py-DA*** *at 470 nm.*

Py-DA with 1,4-DAB:

Table S4. Change of $A_{0\text{-}0}$/ $A_{0\text{-}1}$ and $I_{545(TS)}/I_{470\ (\mathbf{Py\text{-}DA})}$ ratio for **Py-1,4-DAB** conjugate with time.

Time/ min	$A_{0\text{-}0}/A_{0\text{-}1}$	$I_{545(TS)}/ I_{470(Py\text{-}DA)}$
0	0.75	2.42
2.5	0.89	8.63
5.0	0.96	9.41
7.5	0.99	8.67
10.0	1.01	7.07
12.5	1.03	5.26
15.0	1.03	4.44
17.5	1.03	3.66
20.0	1.04	3.00
25.0	1.04	2.05
30.0	1.04	1.44
35.0	1.05	1.07
40.0	1.06	0.78

Note: *$A_{0\text{-}0}$ and $A_{0\text{-}1}$ are the absorbance corresponding to 353 nm and 337 nm respectively. I_{545} – intensity of transient species (TS) at 545 nm and I_{470} – intensity of* ***Py-DA*** *at 470 nm.*

Py-DA with 1,5-DAP:

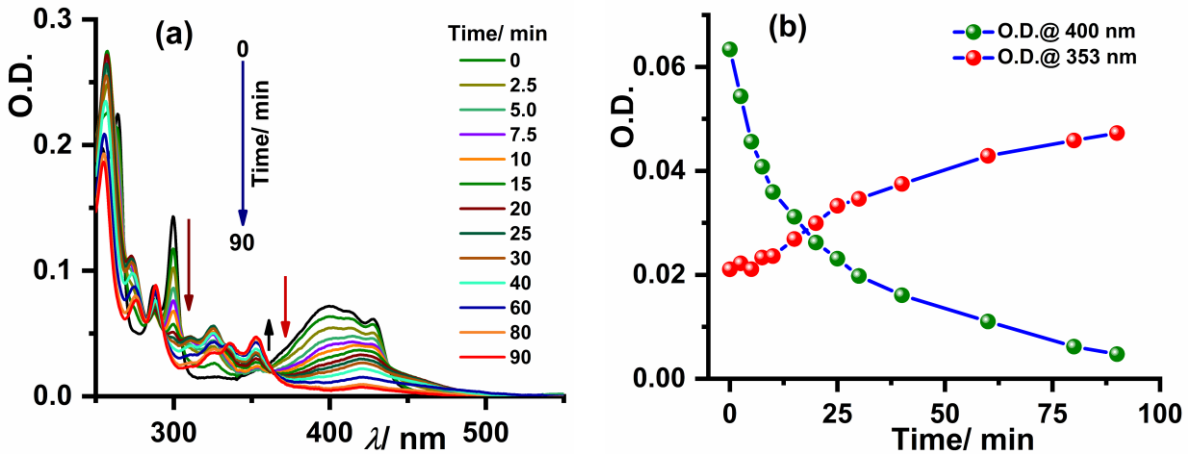


Fig. S31 (a) Time-dependent absorption spectra of **Py-DA** (5 μM) - 1,5-DAP (10 μM) showing change of absorbance, (b) representation of change of O.D. of **Py-DA** with time monitored at both 400 nm and 353 nm.

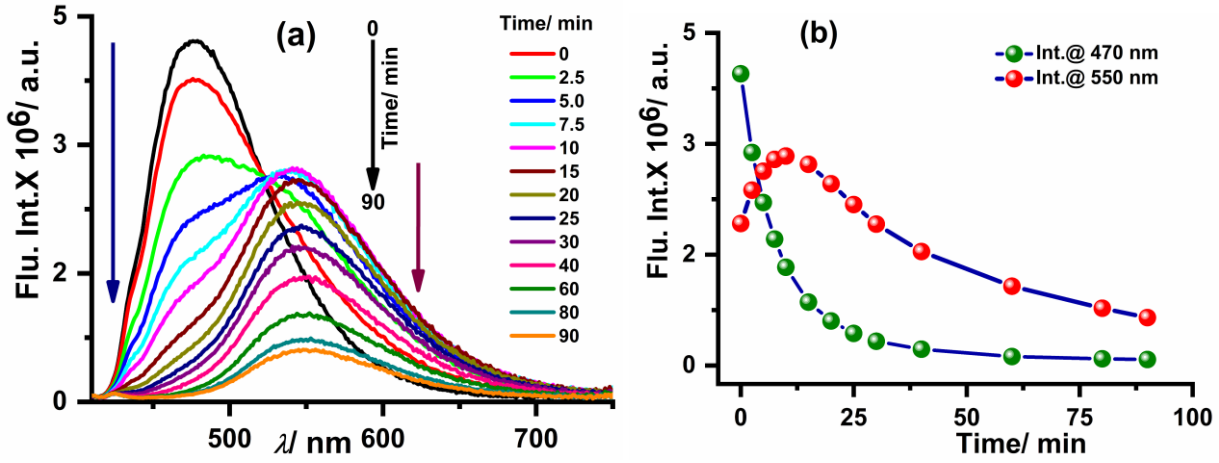


Fig. S32 (a) Time-dependent emission spectra of **Py-DA** (5 μM) - 1,5-DAP (10 μM) showing the change of spectra, (b) representation of change of intensity at both 470 nm and 550 nm band with time.

Table S5. Change of $A_{0\text{-}0}$/ $A_{0\text{-}1}$ and $I_{550(TS)}$/ $I_{470(\textbf{Py-DA})}$ ratio for **Py-1,5-DAP** conjugate with time.

Time/ min	$A_{0\text{-}0}$/ $A_{0\text{-}1}$	$I_{550(TS)}$/ $I_{470(\textbf{Py-DA})}$
0	1.23	0.48
2.5	1.03	0.82
5.0	0.90	1.19
7.5	0.90	1.63
10.0	0.89	2.13
15.0	0.88	3.17
20.0	0.91	4.08
25.0	0.91	5.01
30.0	0.93	5.83
40.0	0.97	7.00
60.0	1.04	8.86
80.0	1.08	8.55
90.0	1.10	8.05

Note: $A_{0\text{-}0}$ and $A_{0\text{-}1}$ are the absorbance corresponding to 354 nm and 337 nm respectively. *I_{550} – intensity of transient species (TS) at 550 nm and I_{470} – intensity of* ***Py-DA*** *at 470 nm.*

Py-DA with spermidine:

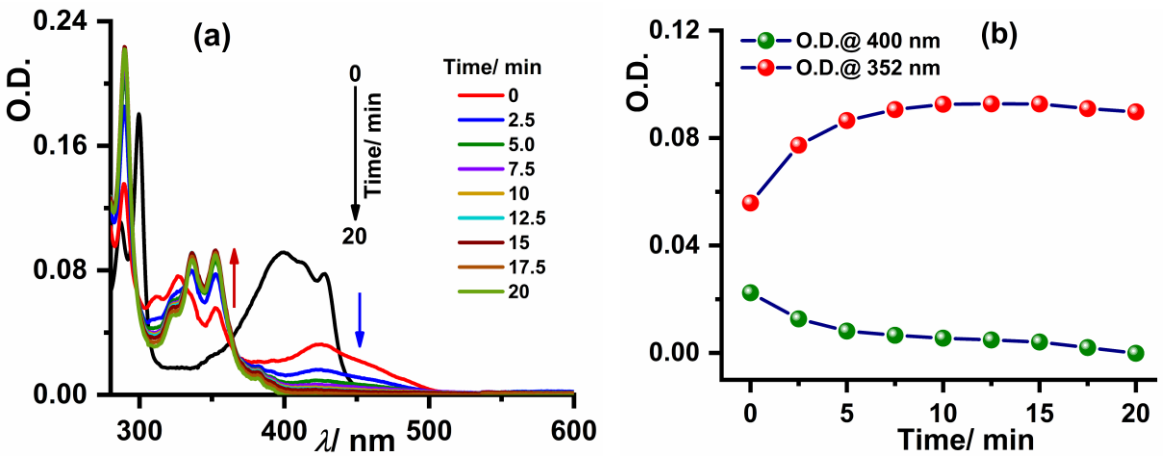


Fig. S33 (a) Time-dependent absorption spectra of **Py-DA** (5 μM) - spermidine (10 μM) showing change of absorbance, (b) representation of change of O.D. of **Py-DA** with time monitored at both 400 nm and 352 nm.

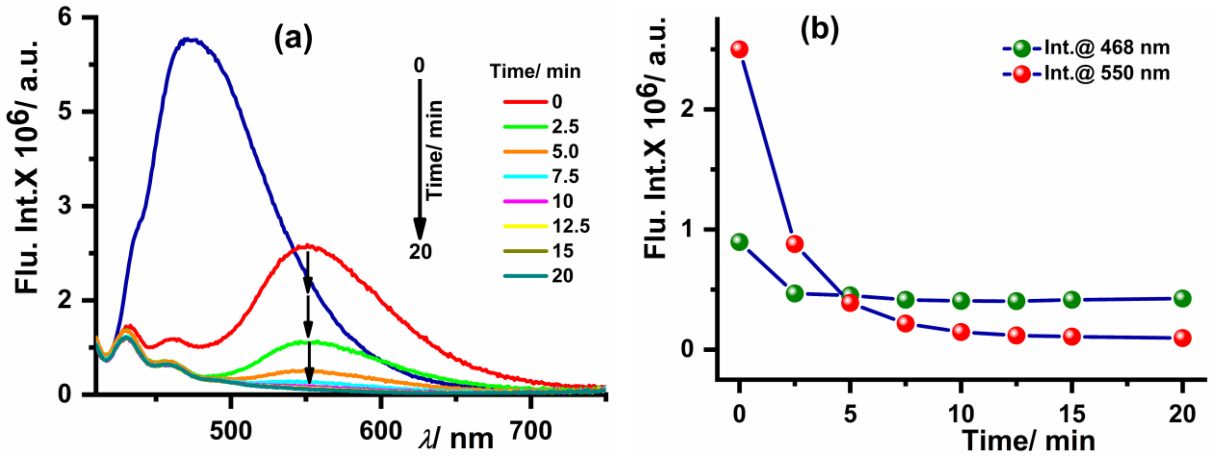


Fig. S34 (a) Time-dependent emission spectra of **Py-DA** (5 μM)-spermidine (10 μM) showing the change of spectra, (b) representation of change of intensity at both 468 nm and 550 nm band with time. Here, we did not observe spectral rise at 550 nm band like other conjugates because of low intensity of 550 nm band.

Table S6. Change of $A_{0\text{-}0}$/ $A_{0\text{-}1}$ and $I_{550(TS)}$/ $I_{468(\textbf{Py-DA})}$ ratio of **Py-Spermidine** conjugate with time.

Time/ min	$A_{0\text{-}0}/A_{0\text{-}1}$	$I_{550(TS)}/ I_{470(Py\text{-}DA)}$
0	0.912	2.791
2.5	0.985	1.884
5	1.009	0.861
7.5	1.019	0.523
10	1.025	0.362
12.5	1.022	0.292
15	1.028	0.261
17.5	1.036	-
20	1.045	0.226

Note: *$A_{0\text{-}0}$ and $A_{0\text{-}1}$ are the absorbance corresponding to 354 nm and 337 nm. I_{550} – intensity of transient species (TS) at 550 nm and I_{468} – intensity of* ***Py-DA*** *at 468 nm.*

Table S7. Summary of average fluorescence lifetime along with the contribution of components for **Py-1,4-DAB** conjugate.

Time (min)	τ_1 (ns)/ cont. (%)	τ_2 (ns)/ cont. (%)	τ_3 (ns)/ cont. (%)	τ_{avg} (ns)
0	11.9/ 4.05	23.6/ 95.95	*a*	23.4
5	5.1/ 7.0	22.8/ 93.0	*a*	22.5
10	5.3/ 14.53	22.6/ 65.56	0.2/ 19.91	21.7
15	8.4/ 27.53	23.9/ 61.25	2.46/ 11.22	21.5
20	7.4/ 28.64	23.7/ 64.27	2.32/ 7.09	21.5
30	8.3/ 30.89	24.0/ 58.47	2.5/ 10.64	21.3
40	10.1/ 25.53	24.0/ 56.0	3.5/ 18.46	20.9

Note: *[a].At t = 0 and 5 min, the conjugate showed bi-exponential decay, hence the third component was absent. The higher average lifetime values of* ***Py-1,4-DAB*** *conjugate was originated from the contribution of longer-lived component (excimer species). The contribution of the longer-lived component was also gradually reduced with increasing time which led to diminishing of an overall average lifetime for this conjugate. Here, the abbreviation cont. is used to denote the contribution.*

Temperature-dependent study of Py-DA excimer in DMSO:

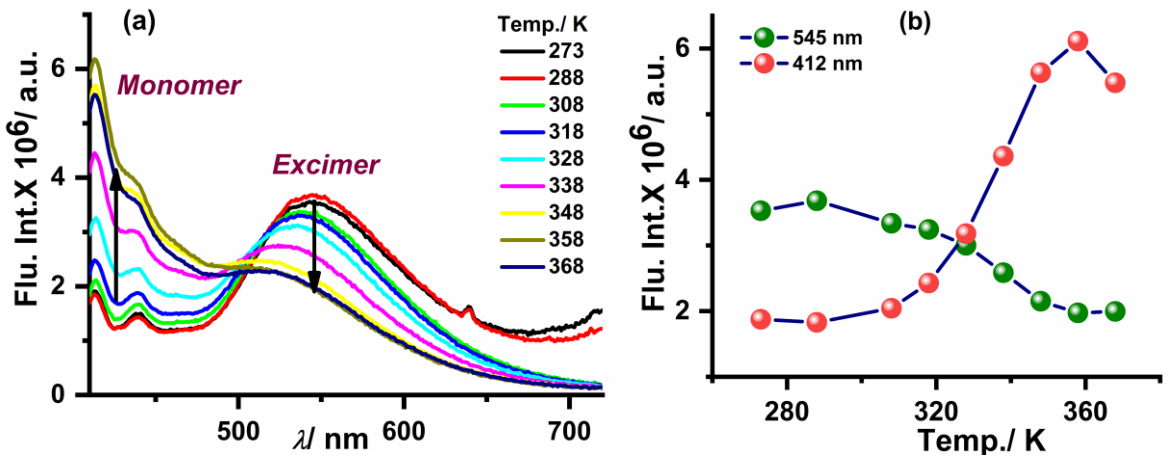
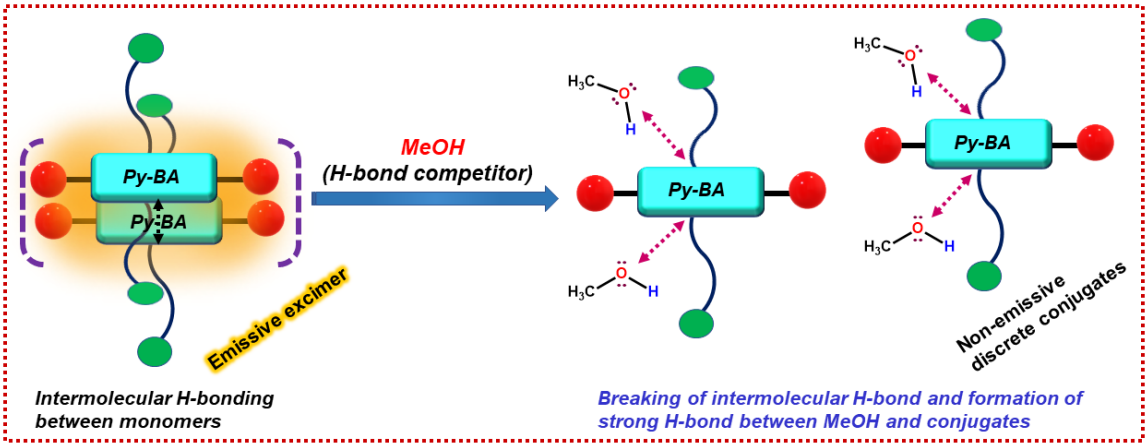


Fig. S35 (a) Temperature-dependent emission spectra of **Py-DA** (50 μM) in DMSO, (b) representation of intensity change at 545 nm and 412 nm band with increasing temperature in DMSO.



Scheme S3 Representation of H-bonding interaction between Py-BA conjugates and effect of MeOH.

Disassembly process of Py-1,3-DAP excimer:

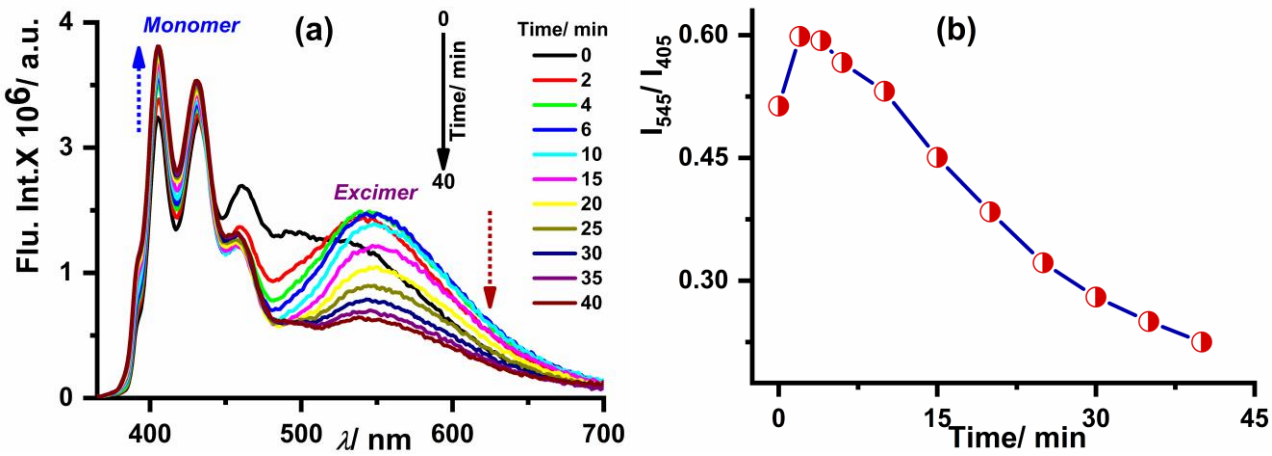


Fig. S36 (a) Time-dependent emission of Py-1,3-DAP conjugate in $CHCl_3$ collected on exciting at 355 nm, (b) representation of change of I_{545} (excimer) to I_{405} (monomer) ratio with time.

Fluorescence study of Py-DA with TEA:

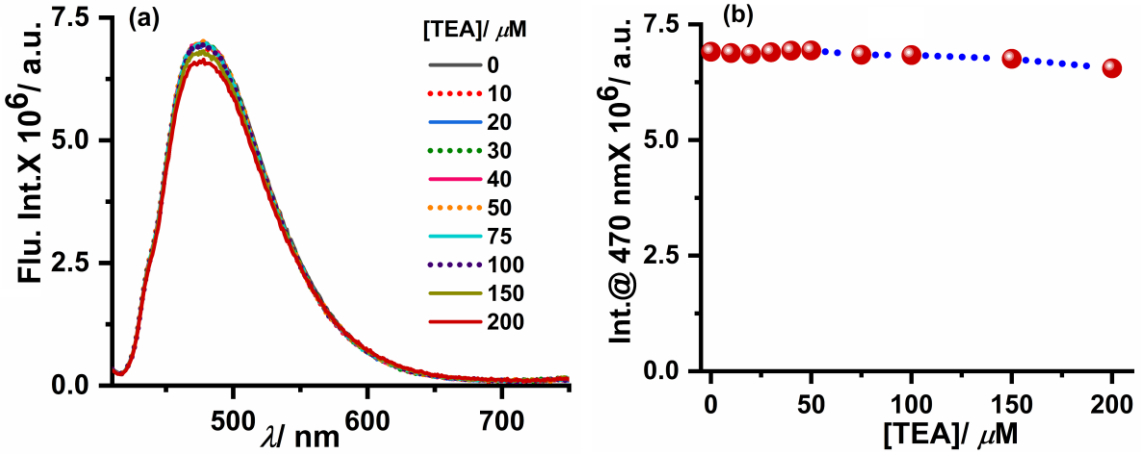


Fig. S37 (a) Fluorescence spectra of **Py-DA** (5 μM) in $CHCl_3$ in presence of triethylamine with varying concentration, (b) plot of 470 nm band intensity *vs* concentration of triethylamine.

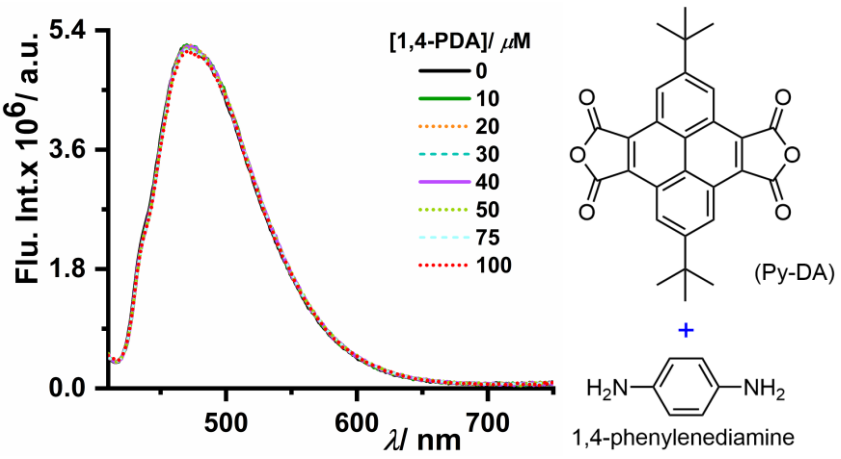


Fig. S38 Left: Emission spectra of **Py-DA** (5 μM) with 1,4-phenylenediamine (0-100 μM) in $CHCl_3$, showing no change in emission, right: chemical structures of **Py-DA** and 1,4-phenylenediamine.

Effect of local environments on assembly and disassembly

It is well-documented in the literature, pyrene excimer is very sensitive towards the local environments (solvent polarity, concentration) and external stimuli. To find out the role of solvent polarity, a few non-polar and polar solvents were chosen considering the feasibility of anhydride- amine reaction in terms of good solubility of both compounds in those solvents. ***Figure 39a*** *disclosed, on increasing solvent polarity, the intensity of excimer band diminished accompanied with showing a considerable bathochromic shift in their emission spectra. The excimer band in relatively polar solvent acetone was mostly positioned at 573 nm whereas it exhibited maximum intensity at 545 nm in $CHCl_3$, proclaiming positive solvatochromic-type behavior of* ***Py-1,4-DAB*** *excimer species. This solvatochromic-type characteristic emerged in the excited state because of polar nature of the conjugate and accordingly its interaction with the surrounding dielectric medium. The fluorescence lifetime of excimer band measured in different solvents (as depicted in* ***Figure 39b****) revealed that τ_{avg} was obtained as the highest in $CHCl_3$ (23.4 ns) and THF (23.4 ns) which showed a regular decrease with increasing solvent polarity (τ_{avg} = 21.2 ns, 19.7 ns and 15.4 ns in DCM, EtOAc and acetone respectively). So, the drop of excimer emission and alleviation of the lifetime in polar solvents delineated, polar-aprotic solvents favoured non-radiative decay on the accounts of specific solvent effect such as H-bonding interaction*

*between **Py-1,4-DAB** and those solvents (schematically represented in **Figure 39c**), which was also proposed by Prasad and co-worker.[69] Following the assembly, we also verified the effect of temperature and viscous medium on the disassembly process. At a relatively higher temperature, the disassembly process became faster which is described in detail in ESI (**Figure S40**). To know the effect of viscous medium, the emission spectra of **Py-1,4-DAB** conjugate in polymethyl methacrylate i.e., PMMA (200 mg/ mL) mixed $CHCl_3$ solution were measured at 295 K. This showed a minimal decrease of excimer band intensity at 545 nm even after 60 min, as shown in **Figure S41a-b**. In absence of PMMA, the same conjugate registered very fast fluorescence decay within 60 min (see **Fig. S42**). The*

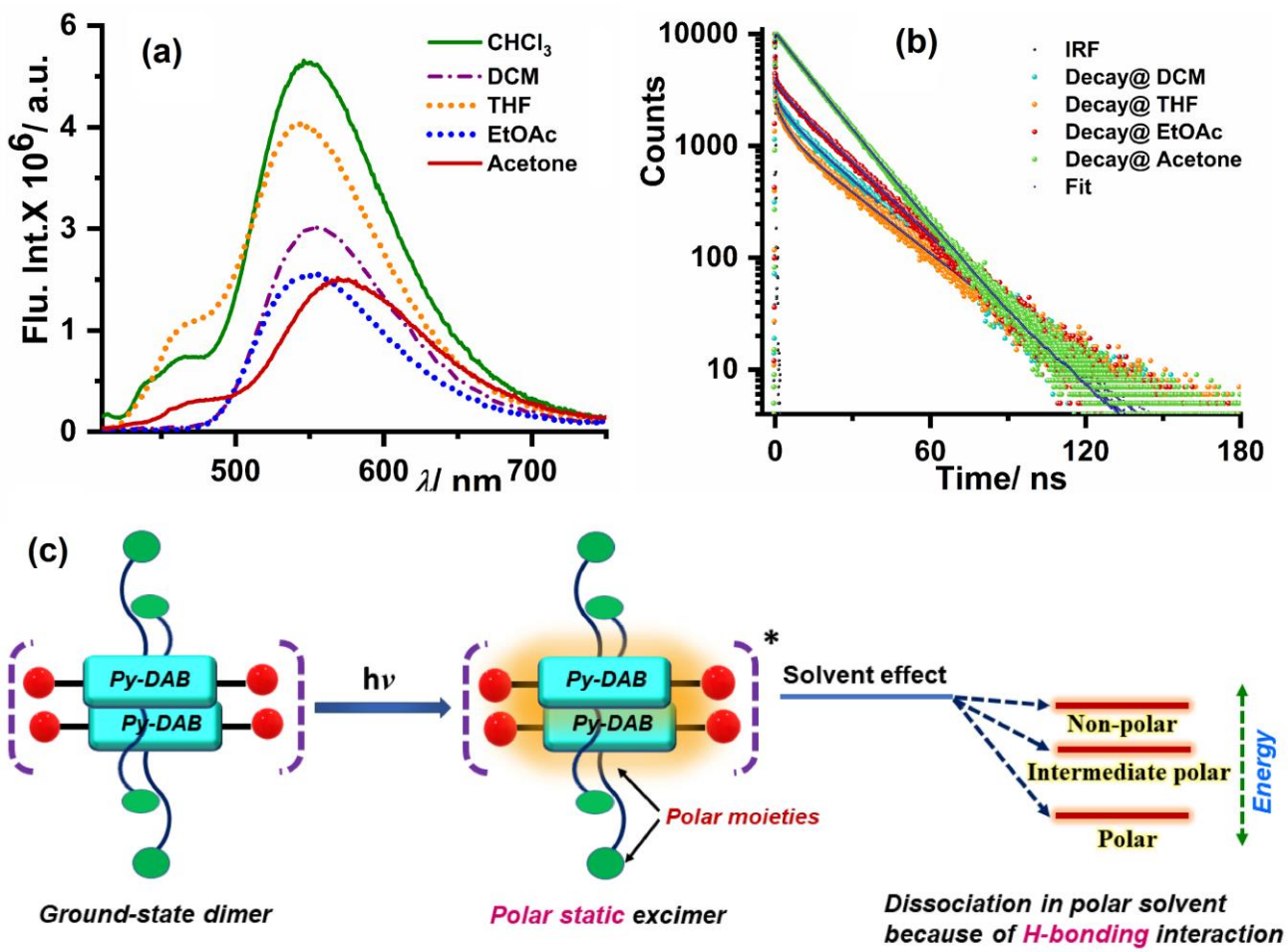


Fig. S39 (a) Emission spectra of **Py-1,4-DAB** excimer in different solvents mentioned in inset (b) Time-resolved fluorescence decay profile of **Py-1,4-DAB** conjugate monitored at respective excimer band in those solvents. (c) Schematic representation of formation of static excimer and effect of solvents on stabilization of excimer species.

highly viscous PMMA medium attenuated the dissociation process of pre-arranged dimers or aggregates by restricting their molecular movements in a confined polymeric environment, thus augmenting the stabilization of excimer inversely, which is schematically depicted in ***Scheme S4****.*

Effect of temperature on disassembly process:

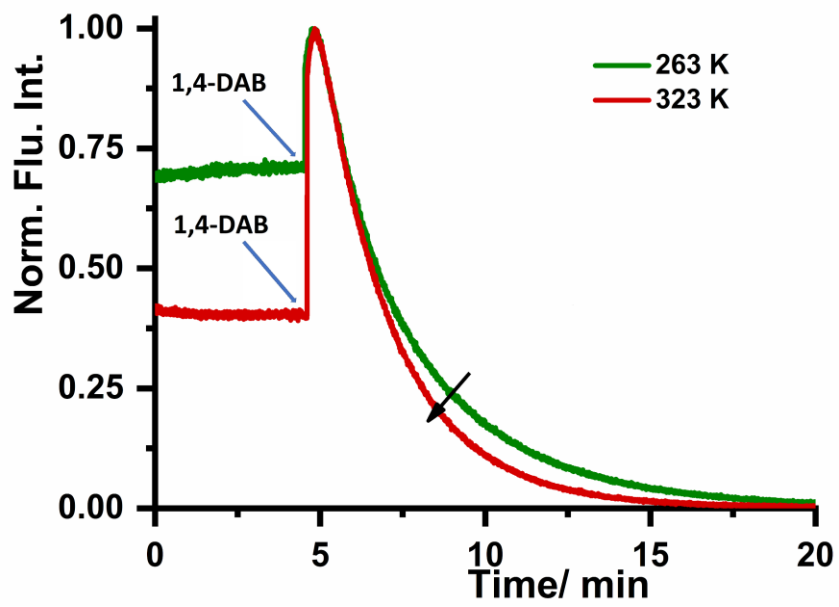


Fig. S40 Fluorescence kinetics of **Py-1,4-DAB** conjugate in $CHCl_3$ carried out at very low (263 K) and high temperature (323 K); kinetics was monitored at 545 nm excimer band.

Note: *To get an insight into the sensitivity of such disassembly process towards thermal energy, we performed the fluorescence kinetics at low (263 K) and moderately high temperature (323 K) in* $CHCl_3$*. The kinetics results demonstrated a noticeable difference in the exponential decay of fluorescence quenching between low and high temperatures. The rate of fluorescence quenching became faster at high temperature, indicating high thermal energy facilitated the dissociation of H-bonded dimers than low temperature. Oppositely, we could surmise, low temperature increased the stability of dimer species spawning to slow decay in the kinetics. Thus, this study established the dependence of excimer disassembly on thermal energy for such conjugates.*

Effect of viscous medium on self-assembly process:

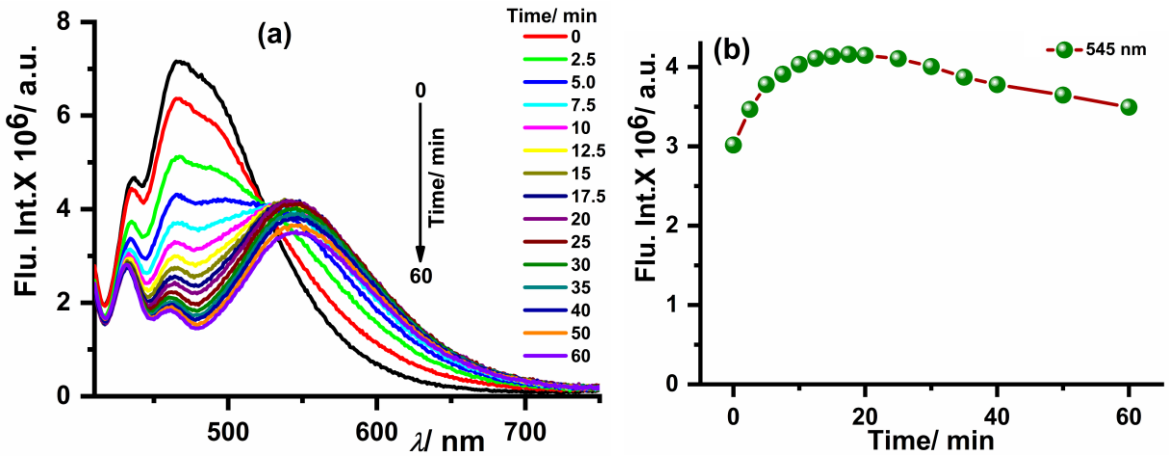


Fig. S41 (a) Time-dependent emission spectra of **Py-1,4-DAB** conjugate in PMMA (200 mg/ mL) mixed $CHCl_3$, (b) representation of change of intensity at 545 nm excimer band with time in presence of PMMA.

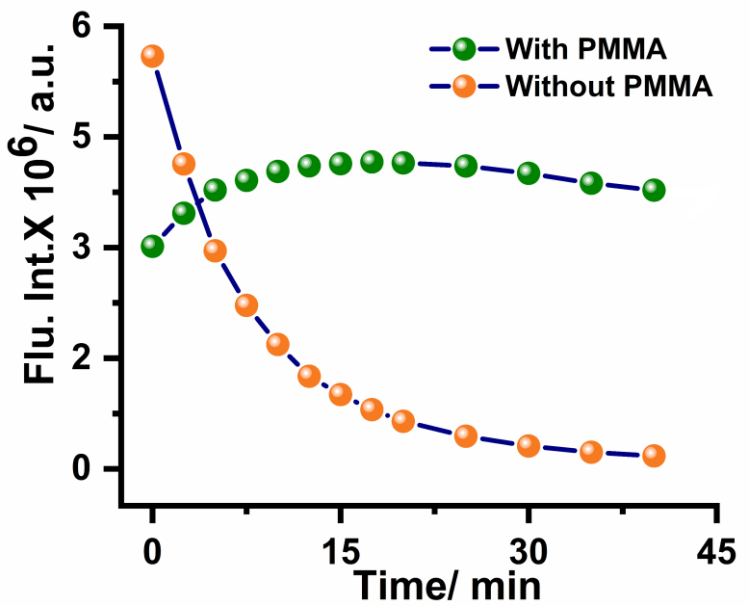
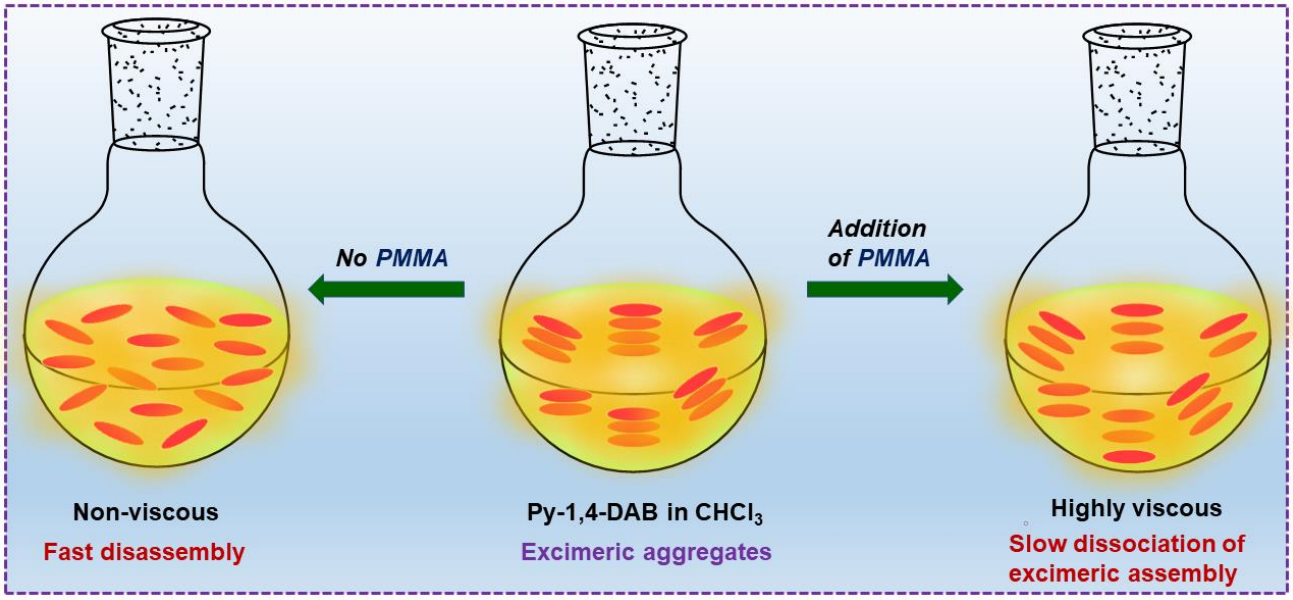
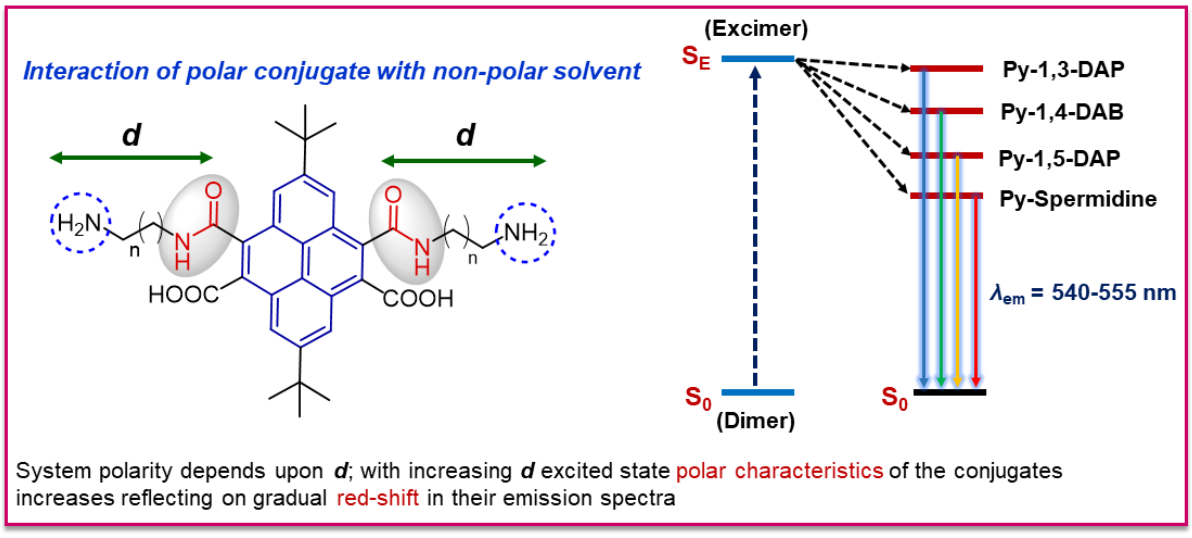


Fig. S42 Representation of change in 545 nm excimer band intensity with time in presence (green dots) and absence (orange dots) of PMMA polymer.

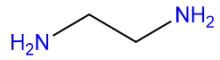
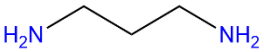
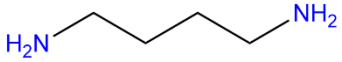
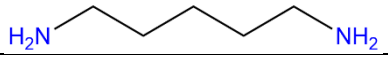
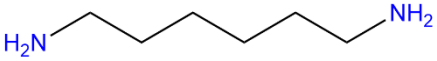
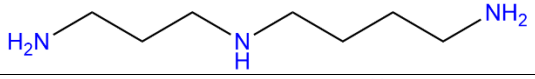
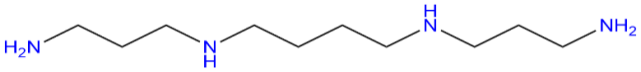


Scheme S4. Illustration of effect of viscous medium on disassembly of **Py-1,4-DAB** aggregates – (left) without PMMA and (right) in presence of PMMA.



Scheme S5. Illustration of origin of polarity and distance between polar moieties in the structural skeleton of monomeric Py-BA conjugates (left); representation of splitting of excited-state energy for the conjugates with varying alkyl chain length along with their corresponding transitions from excimer to ground state.

Table S8. Structure of BAs and their corresponding p*K*a values.[6-8]

Biogenic Diamine	Structures	*p*Ka
Ethylenediamine		10.1, 7.0
1,3-Diaminopropane		10.9, 9.8
Putrescine		10.8, 9.4
Cadaverine		10.3, 9.1
1,6-hexanediamine		11.9
Spermidine		10.9, 8.4, 9.9
Spermine		10.9, 8.4, 7.9, 10.1

Comparison of I_E/ I_M ratio with different chain length containing four BAs:

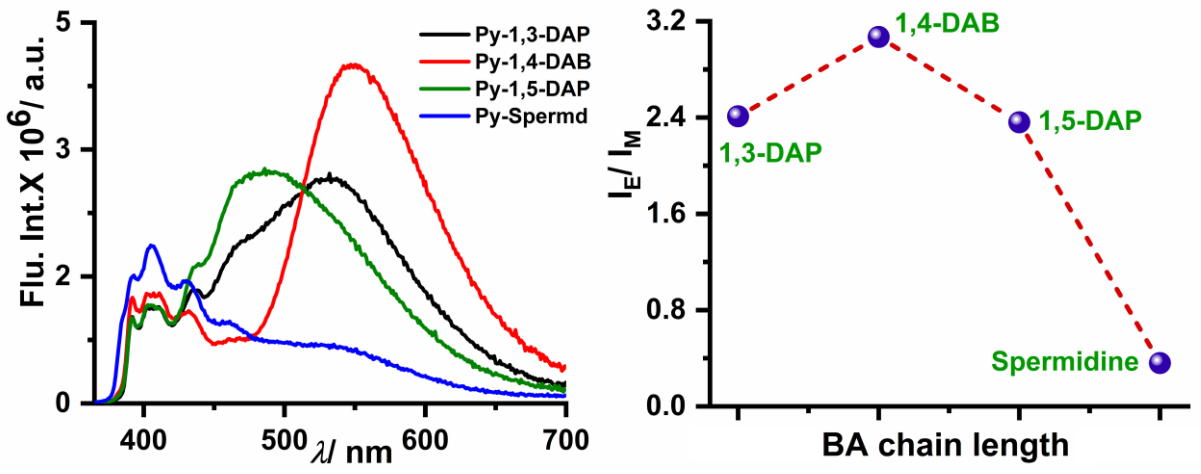


Fig. S43 Emission spectra of Py (5 μM)-BAs (10 μM) conjugates in $CHCl_3$ collected on exciting at 355 nm (left), representation of variation of I_E/ I_M ratio with chain length of BAs (right).

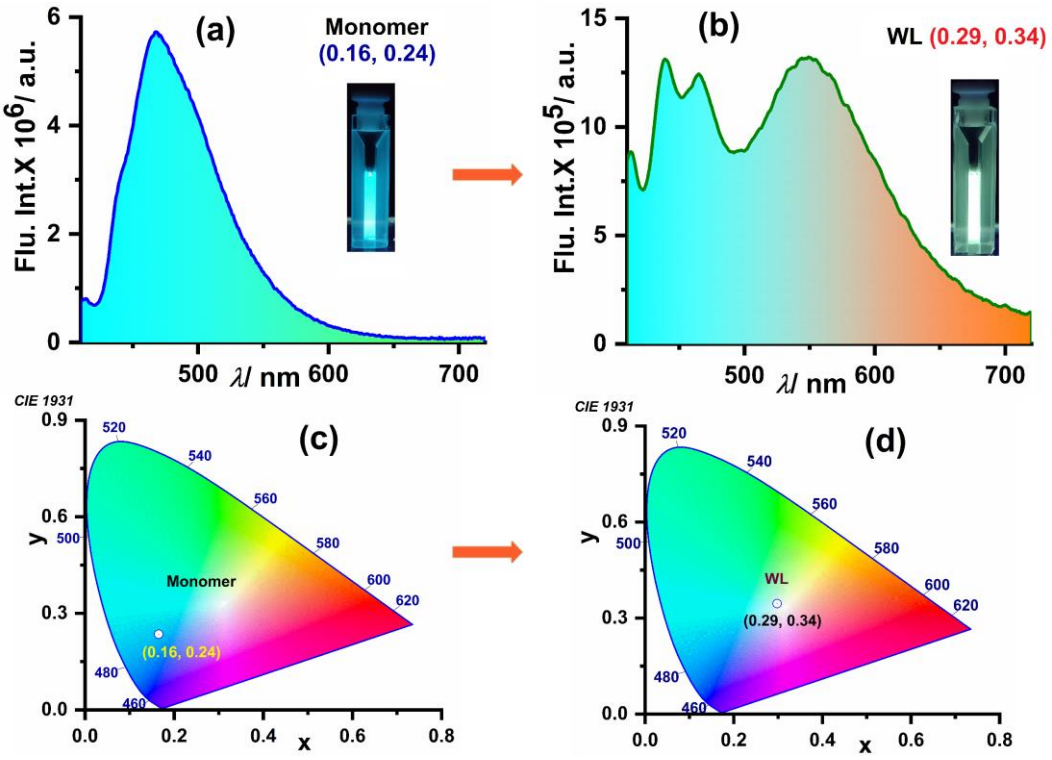


Fig. S44 Emission spectra of (a) **Py-DA** monomer and (b) white light emitting solution of **Py-1,5-DAP** conjugate in $CHCl_3$; inset showing the cuvette images of cyan monomer and white light solution (c) and (d) represent the CIE-coordinates of both solutions in the chromaticity diagram.

Note: *In the concentration-dependent fluorescence study, firstly emission spectra of probe* ***Py-DA*** *(5 μM) was measured showing* λ_{max}^{em} *= 468 nm. After that, N, N-DMPA (concentration range: 5-50 μM) was consequently added in the solution which showed beginning of emergence of new band at 545 nm. At a certain concentration of N, N-DMPA (20 μM), both* ***Py-DA*** *and* ***Py-N, N-DMPA*** *excimer species contributed equally in emission which finally engendered intermediate white-light emission in solution. This same procedure was also followed for* ***Py-1,5-DAP*** *system. So, it can be concluded that intermediate WL was achieved at a specific concentration ratio of 1:4 for* ***Py-DA*** *and N, N-DMPA/ 1,5-DAP respectively.*

Representation of change of CIE with concentration of BA:

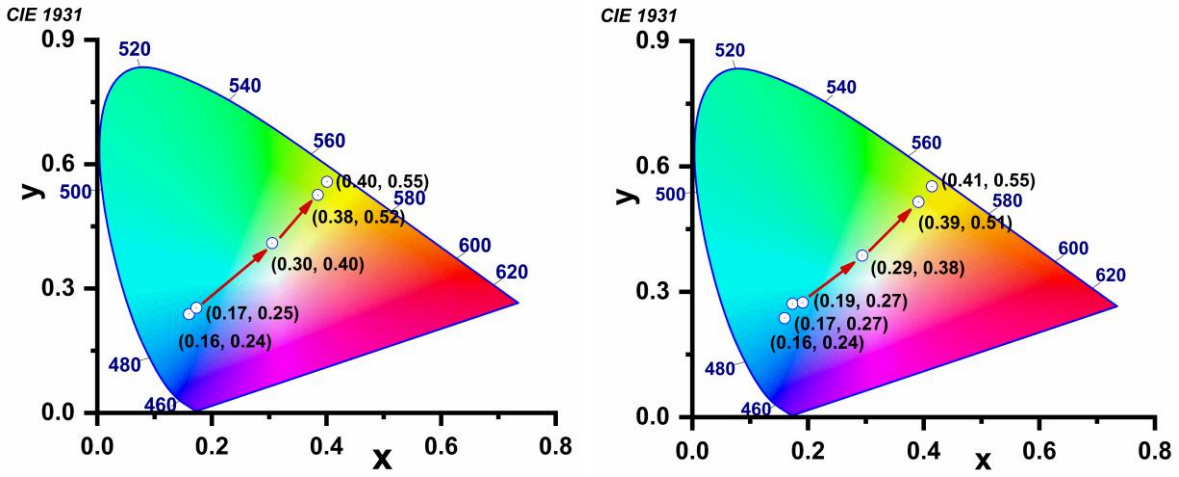


Fig. S45 CIE-diagrams representing the change of CIE-coordinates of (left) **Py-1,4-DAB** conjugate's emission color with concentration; (right) **Py-*N, N*-DMPA** conjugate's emission color with concentration. Concentration of both BAs were considered as 0, 5, 10, 20, 30 and 40 μM respectively.

Note: *The chromaticity diagram shows the smooth change of CIE values from cyan to yellowish-orange region passing via an intermediate white light region.*

Representation of change of CIE with time:

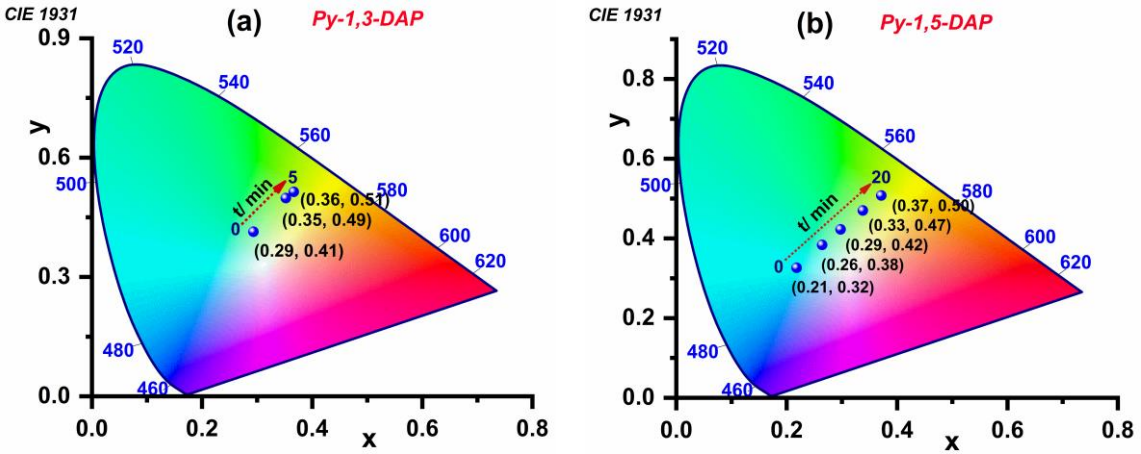


Fig. S46 Representation of CIE change with time for (a) **Py-1,3-DAP** conjugate and (b) **Py-1,5-DAP** conjugate.

Note: *The chromaticity diagrams show a linear change of CIE values with time for Py-1,3-DAP and* ***Py-1,5-DAP*** *complexes. At t = 0 min, i.e., just after addition, CIE for Py-1,3-DAP was obtained as (0.29, 0.41) nearby white-region; whereas* ***Py-1,5-DAP*** *showed CIE value starting from cyan region (0.21, 0.32). This CIE indicates that the response of 1,3-DAP is faster than 1,5-DAP in tuning the CIE at t = 0 min.*

Spectral representation of excimer to monomer transformation *via* disassembly:

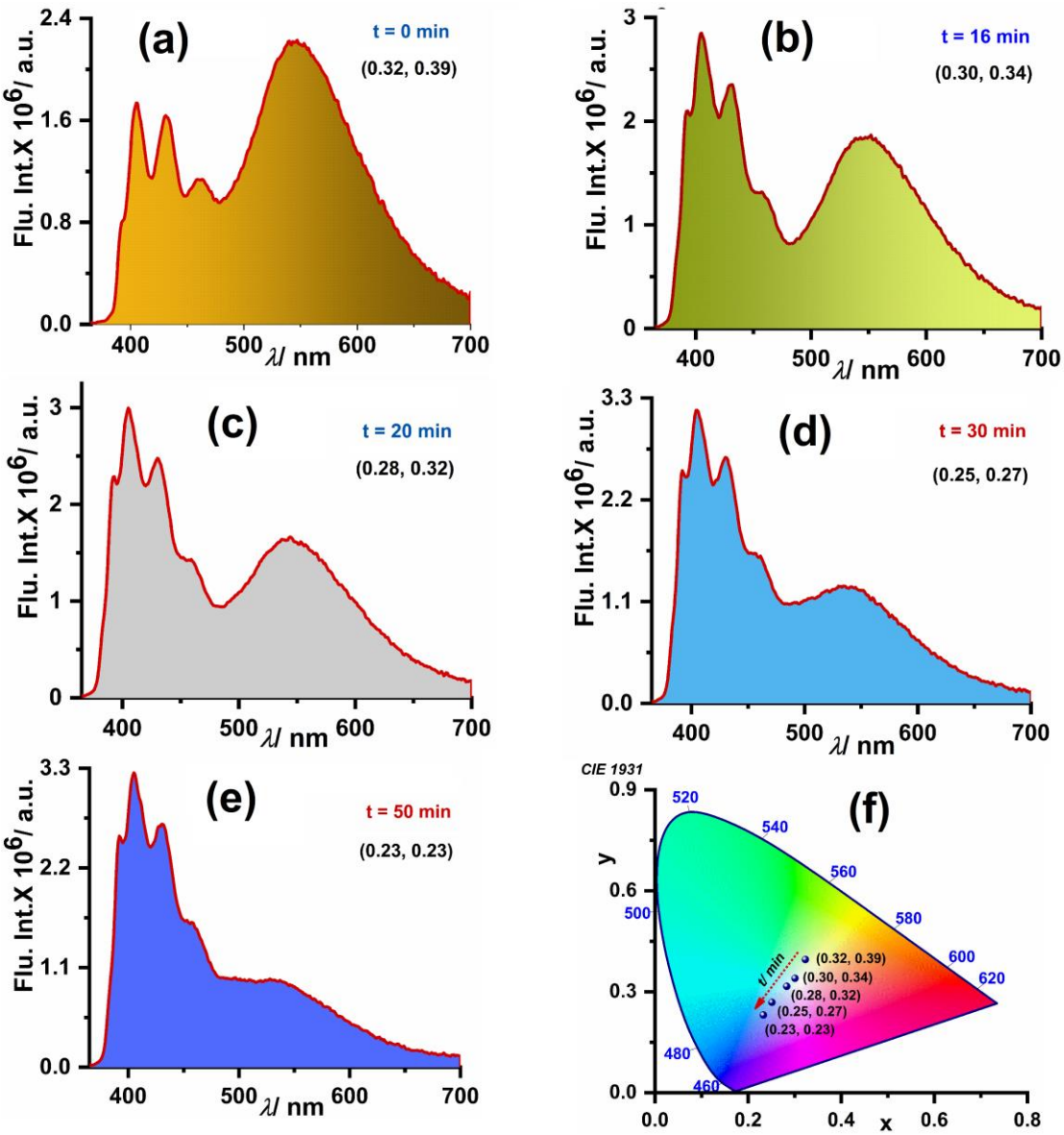


Fig. S47 (a)-(e) Time-dependent change of emission spectrum of **Py-1,4-DAB** conjugate collected on exciting at 355 nm.

Note: *Initially, the excimer band was prominent compared to the monomer band to result in an emission in the yellow region. With time, the excimer band intensity gradually decreased with simultaneous enhancement of monomer intensity which led to altering the CIE values from (0.32, 0.39) to (0.23, 0.23).*

Emission studies in solid-state (thin-film):

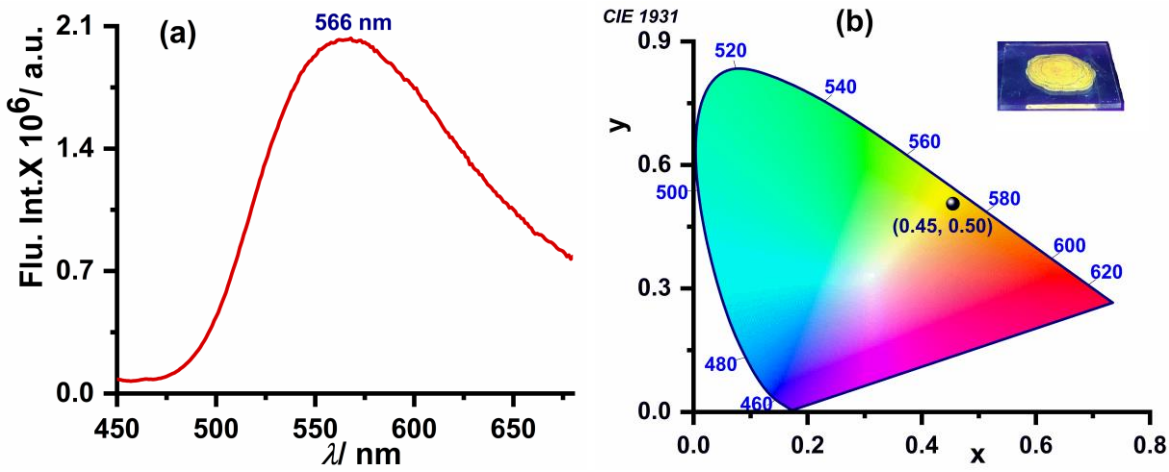


Fig. S48 (a) Solid-state thin film emission spectra of **Py-Spermidine** conjugate (λ_{ex} = 425 nm) (b) Chromaticity diagram representing CIE value of the conjugate; inset represents an image of yellow emissive thin-film captured upon illuminating at 365 nm.

FESEM images of Py-BA conjugates:

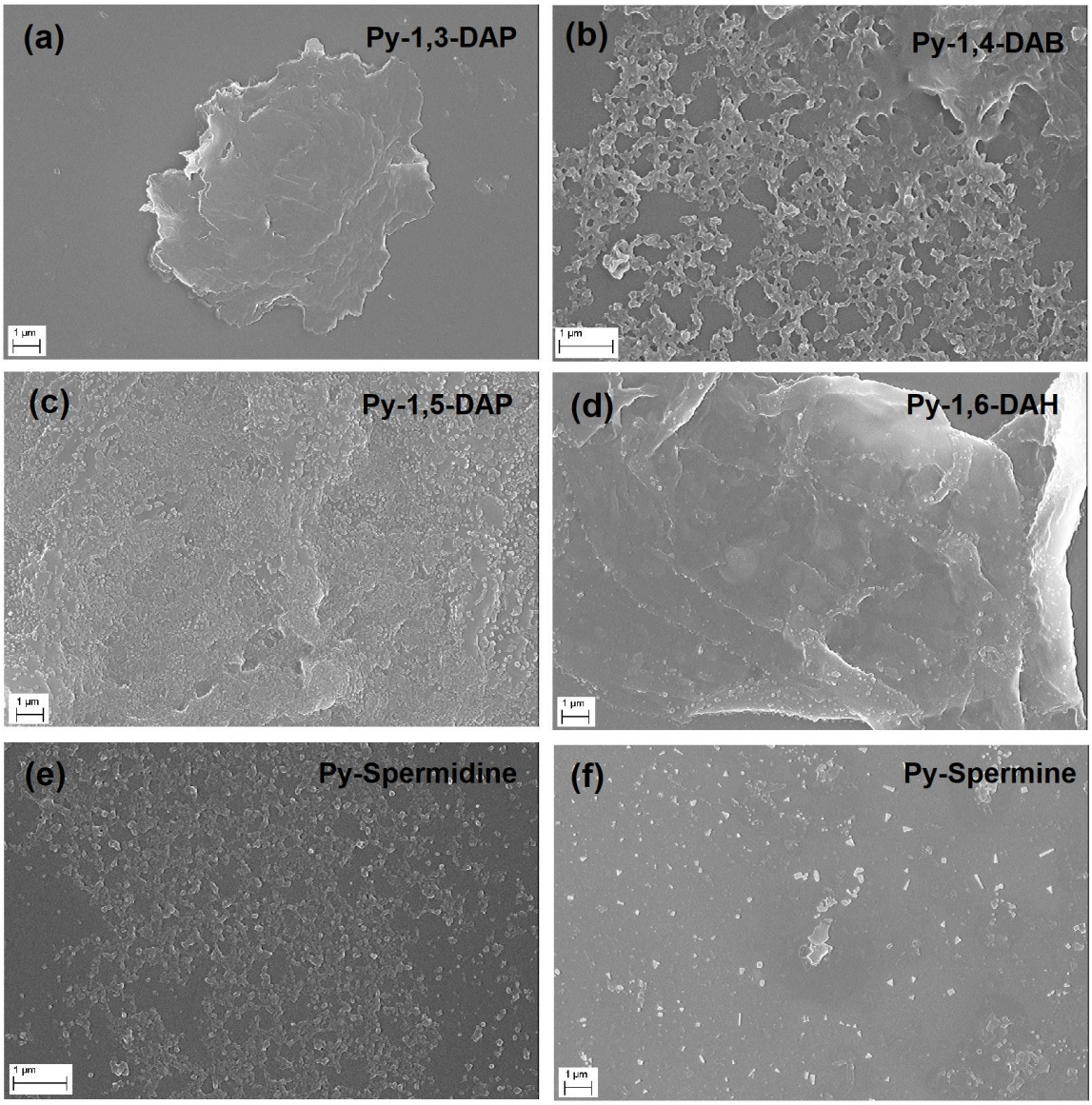


Fig. S49 (a)-(f) SEM images of Py-BA conjugates possessing various alkyl chain length collected at a fixed time; solutions were drop-casted after 10 min of addition of BAs to **Py-DA** solution.

Note: *The rate of disassembly of excimer species was faster for* ***Py-1,4-DAB****,* ***Py-Spermidine*** *and* ***Py-Spermine*** *conjugates where it became slower for Py-1,3-DAP,* ***Py-1,5-DAP*** *and* ***Py-1,6-DAH****. Hence, at t = 10 min, the latter three conjugates existed as large size aggregates which reflected on their SEM images. On the contrary, this aggregates of the other three former conjugates were already dissociated to generate interconnected network morphology (for 1,4-DAB and spermidine) and small size discrete particles (for spermine) at the same time. These SEM pictures provided a better insight into the alkyl-chain length-dependent assembly and disassembly process already established by spectroscopic investigations.*

Py-1,3-DAP conjugate:

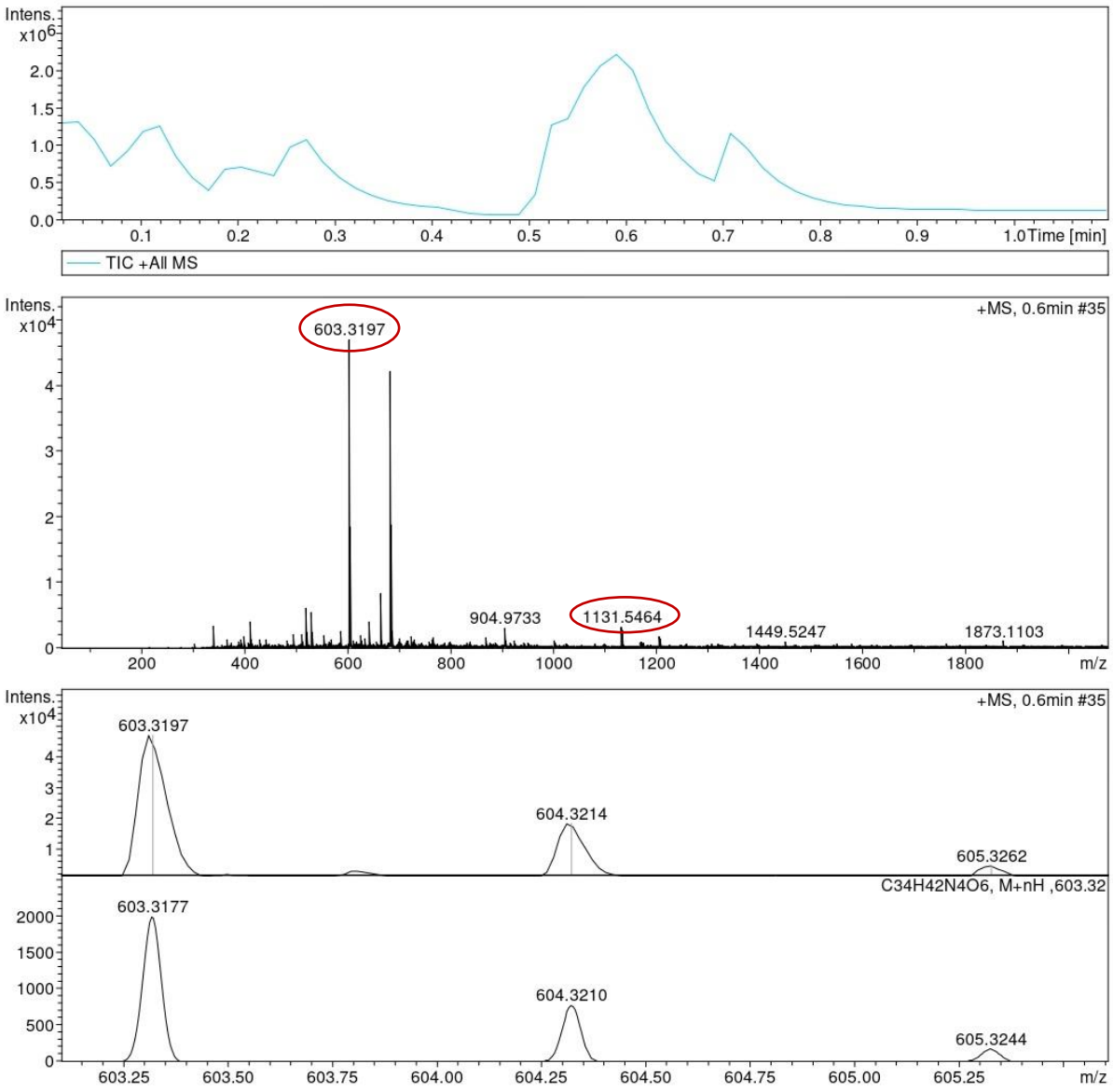


Fig. S50 Chemical structure of **Py-1,3-DAP** conjugate and its ESI mass spectra; **expected mass** - 603.3138 and 1130.5365; **obtained mass** – 603.3197 [M + nH] and 1131.5464 [M + nH].

Py-1,5-DAP conjugate:

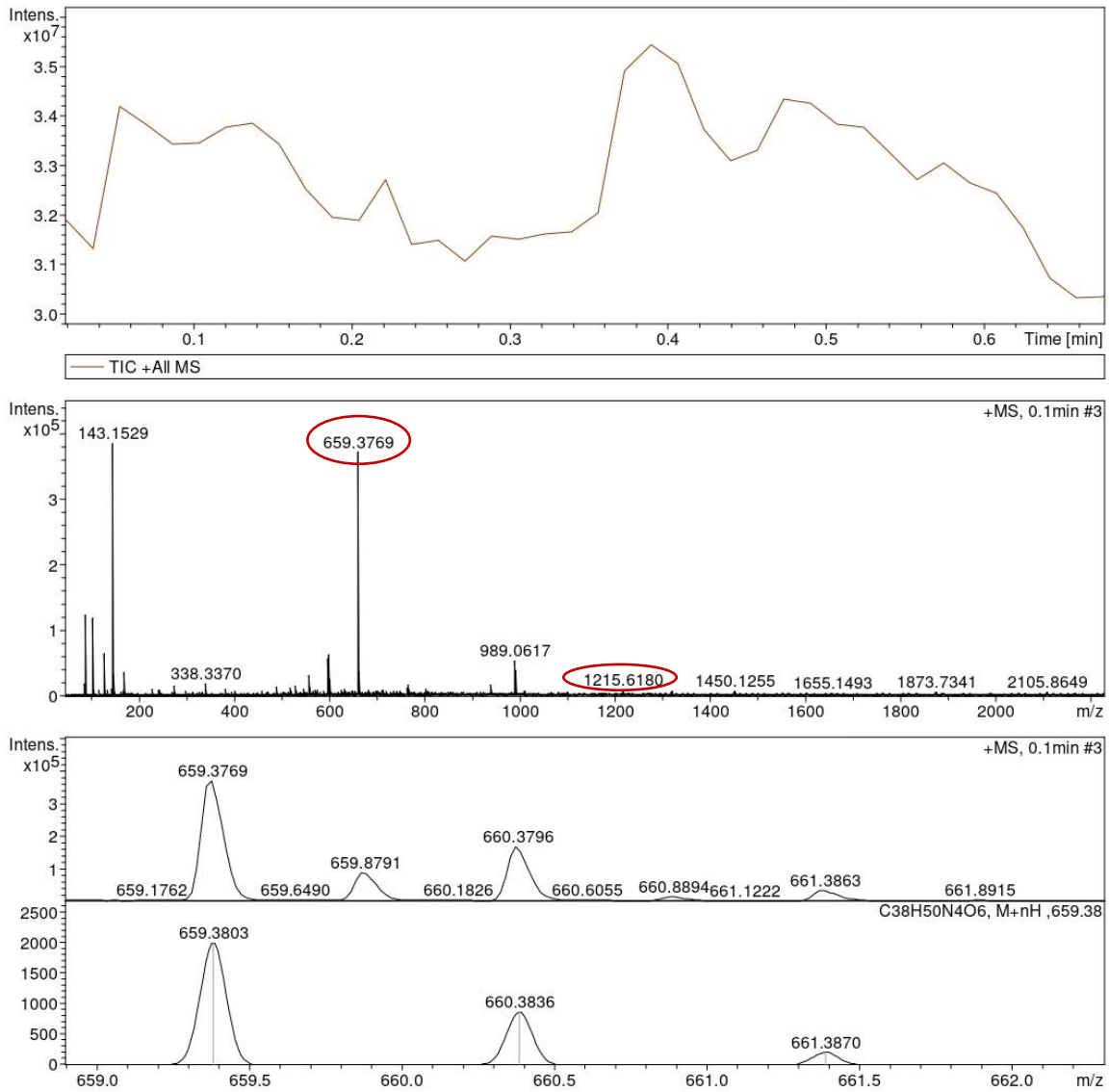


Fig. S51 Chemical structure of **Py-1,5-DAP** conjugate and its ESI mass spectra; **expected mass** – 659.3764 and 1214. 6304; **obtained mass** – 659.3769 [M + nH] and 1215.6180 [M + nH].

Py-*N*, *N*-DMPA conjugate:

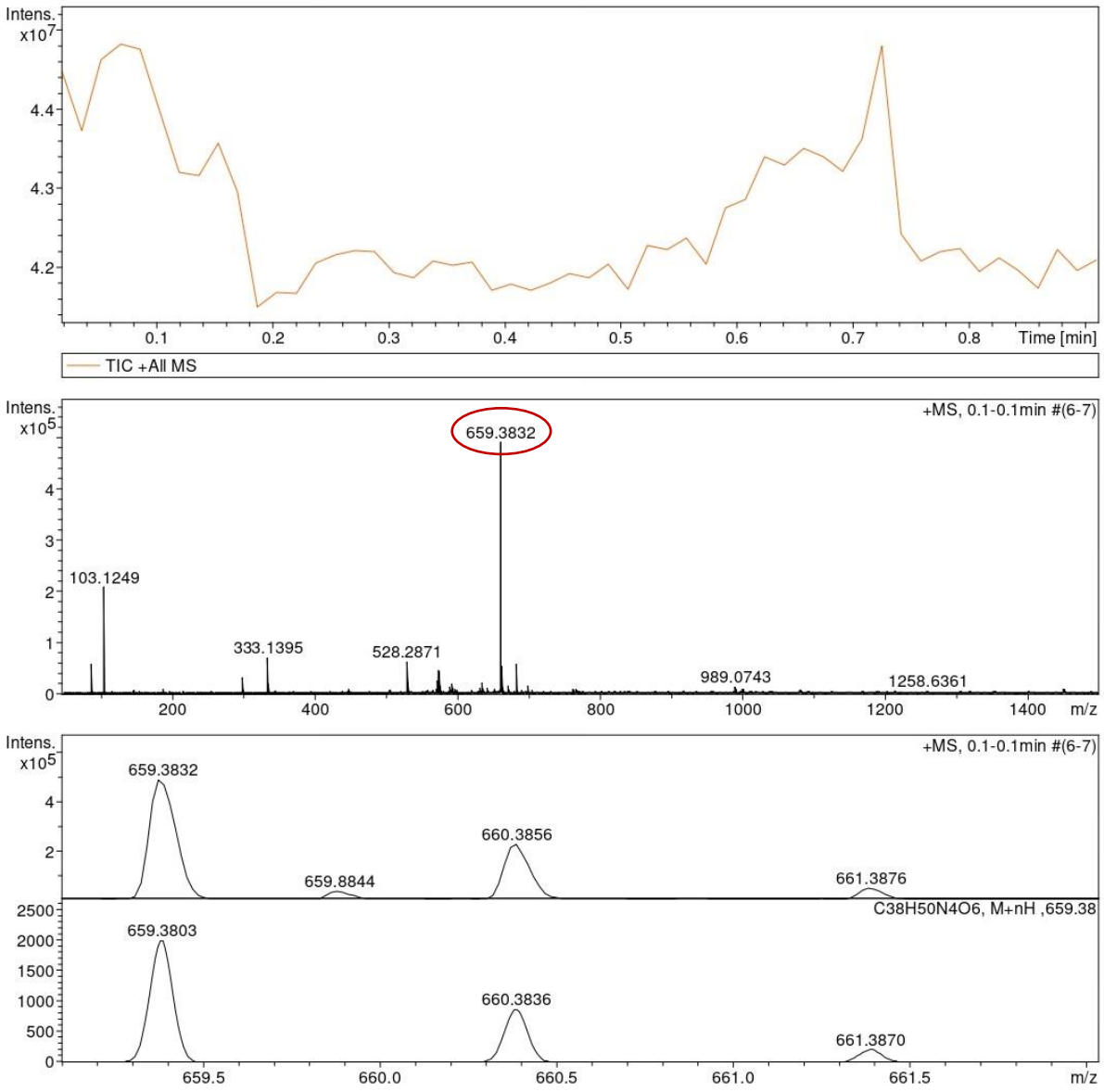


Fig. S52 Chemical structure of **Py-*N*, *N*-DMPA** conjugate and its ESI mass spectra; **expected mass** – 658.3730 and **obtained mass** – 659.3832 $[M+H]^+$.

Py-Spermidine conjugate:

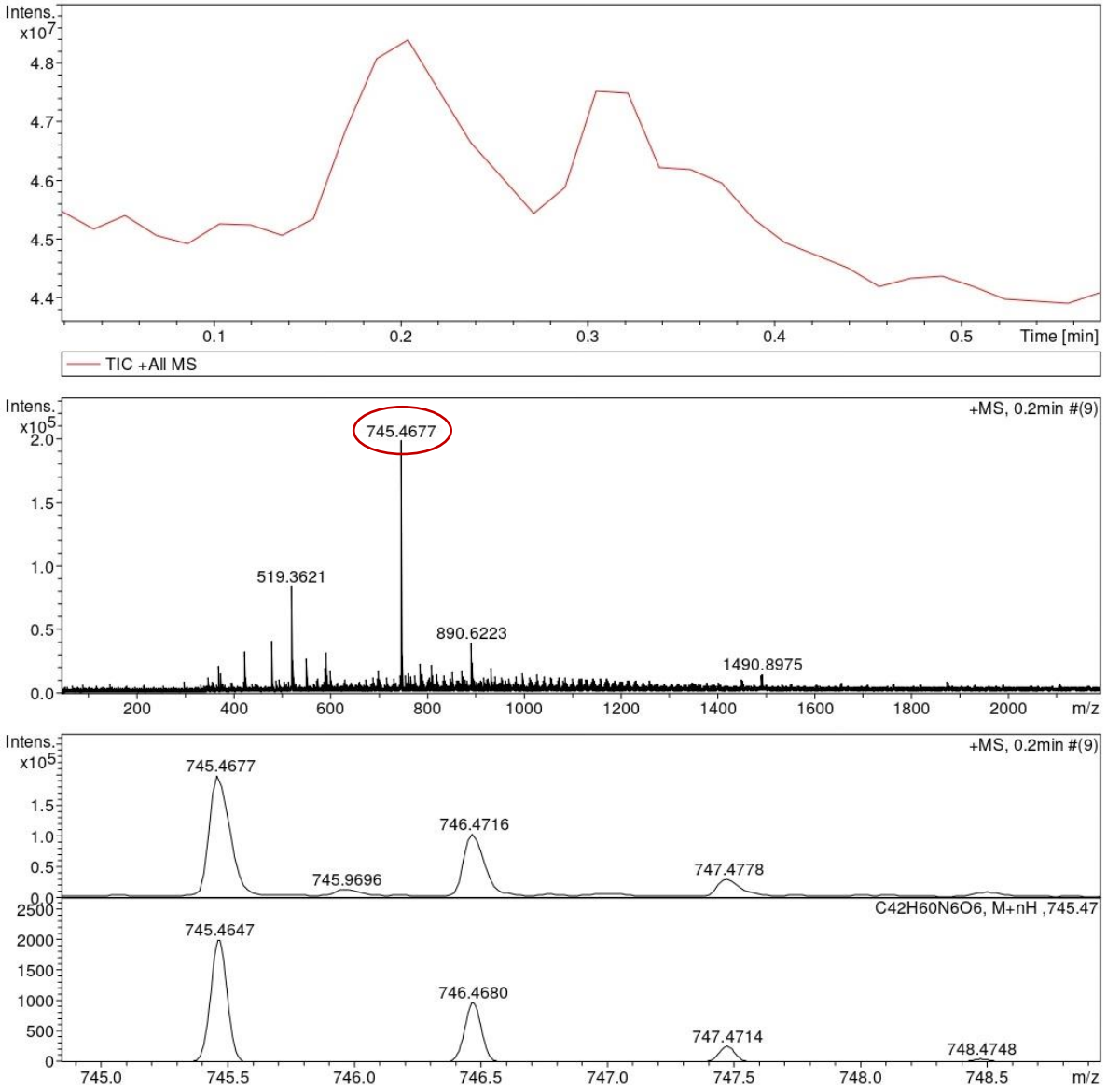


Fig. S53 Chemical structure of **Py-Spermidine** conjugate and its ESI mass spectra; **expected mass** – 744.4574 and **obtained mass** – 745.4677 $[M+H]^+$.

Note: *In this case, the peak corresponding to dimer species could not be detected might be because of very low ionization.*

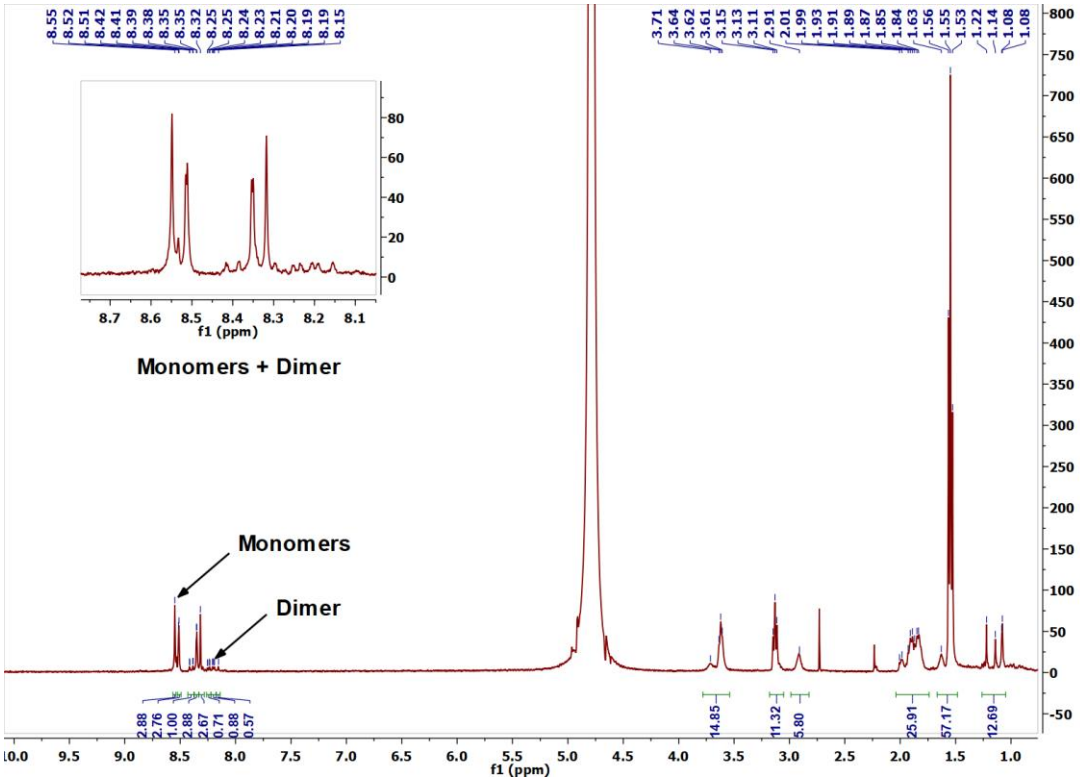


Fig. S54 ^{1}H NMR spectra of **Py-1,4-DAB** conjugate in D_2O recorded at 400 MHz.

Note: *To get an idea about the products formed in solution, we have recorded the ^{1}H NMR spectra of* ***Py-1,4-DAB*** *conjugate (crude) in its good solvent D_2O. The reaction was performed between* ***Py-DA*** *(20 mM) and 1,4-DAB (40 mM) in 1.5 mL $CHCl_3$. When the reaction was completed, the solvent was evaporated and fully dried. Again, in this mixture $CHCl_3$ was added and the precipitate was formed. The precipitate was filtered and washed repeatedly with $CHCl_3$ and pentane, dried under vacuum and we recorded the ^{1}H NMR in D_2O. The compounds were soluble in D_2O. The aromatic protons corresponding to the pyrene core symmetrically split into four closely positioned singlets. Their coupling constant value was seen as very high (14.0 Hz) which did not match with the meta-coupling value between two adjacent protons, ruling out meta-coupling here. Here, there is no possibility of getting the doublet pattern for this conjugate. If only one regioisomer was formed in solution, then we could get two singlets only, no matter it is symmetric or asymmetric product. But here the emergence of four close singlets in the aromatic region indicates a mixture of regioisomers present in solution. Also, if we carefully look at the signals of tert-butyl groups, it showed three closely positioned singlets, the intensity of one singlet is higher than other two singlets. In 2009, Yamato group reported two types of such 4,9- and 4,10-disubstituted pyrene formaldehyde products where they obtained only one singlet corresponding to 18 protons for 4,9-substituted product and two singlets corresponding to two types of 9 protons for 4,10-substituted product* (J.-Y. Hu, A. Paudel, T. Yamato, *J. Chem. Res.*, 2009, 109-113).[9] *We have also observed a similar type of splitting for tert-butyl protons which indicates that only*

*singlet arose from 18 H of 4,9-substituted **Py-1,4-DAB** derivative and two singlets appeared from two types of 9 H in 4,10-substituted **Py-1,4-DAB** derivative. The multiple peaks in aliphatic region arose from unreacted 1,4-DAB and 1,4-DAB conjugated **Py-DA**. Interestingly, we observed multiple low intense peaks with similar splitting than high intense peaks in aromatic region which indicated formation of dimer in addition to monomers conjugates. From the peak ratio of monomer and dimer, the approximate molar ratio of both products (monomers and dimer) is obtained as 86:14. So, monomer conjugates are the major and dimer one is minor products in this reaction.*

IR spectra of Py-DA and Py-1,3-DAP conjugate:

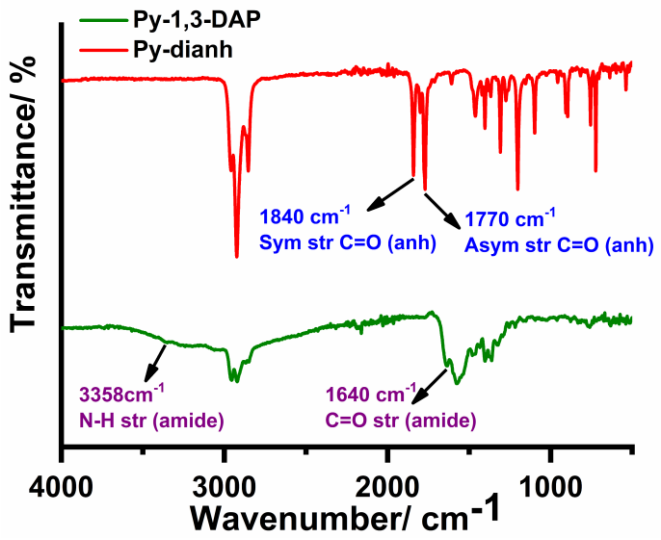
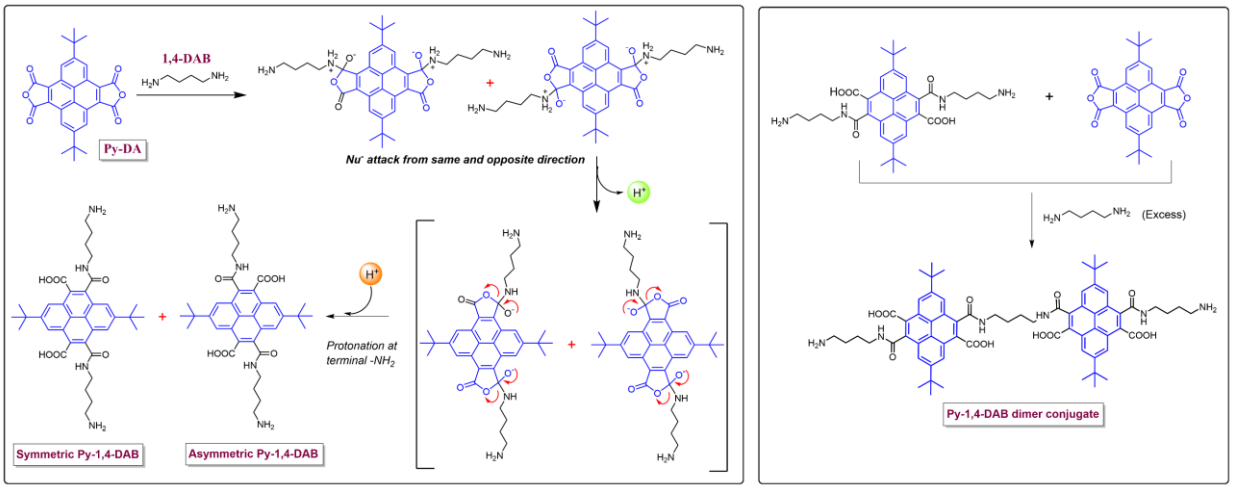


Fig. S55 Comparison of IR spectra between **Py-DA** probe and **Py-1,3-DAP** conjugate in $CHCl_3$.

Possible mechanism for formation of products:



Scheme S6. Representation of the most possible mechanism responsible for formation of the regioisomeric monomers and dimer from **Py-DA** and 1,4-DAB. Left figure demonstrates mechanism for formation of two **Py-1,4-DAB** monomers and right figure depicts **Py-1,4-DAB** dimer formation.

Note: *1,4-DAB occurs nucleophilic attack on anhydride moieties from the same and opposite side to make two open regioisomers. The regioisomer formed in the solution further undergoes nucleophilic reaction with* ***Py-DA*** *in presence of excess 1,4-DAB to form the dimer conjugate.*

E. Theoretical investigations:

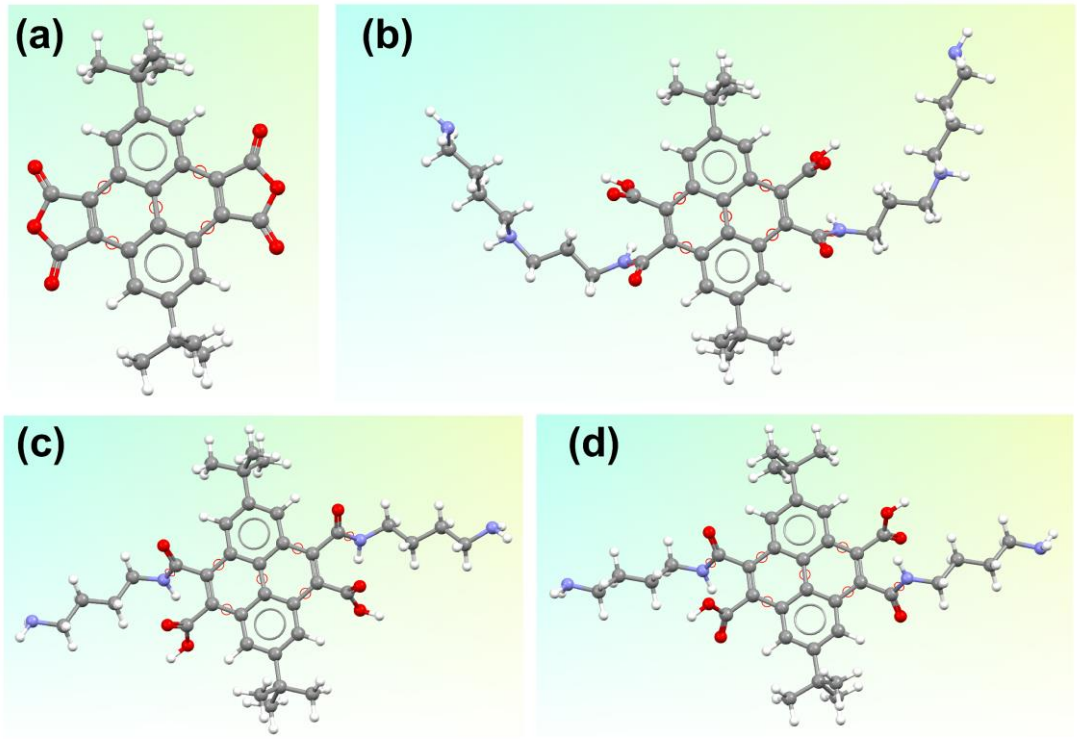


Fig. S56 DFT optimized geometry of monomer species for (a) **Py-DA**, (b) **Py-Spermidine** symmetric (c) **Py-1,4-DAB** symmetric and (d) **Py-1,4-DAB** asymmetric as represented by ball-and-stick model.

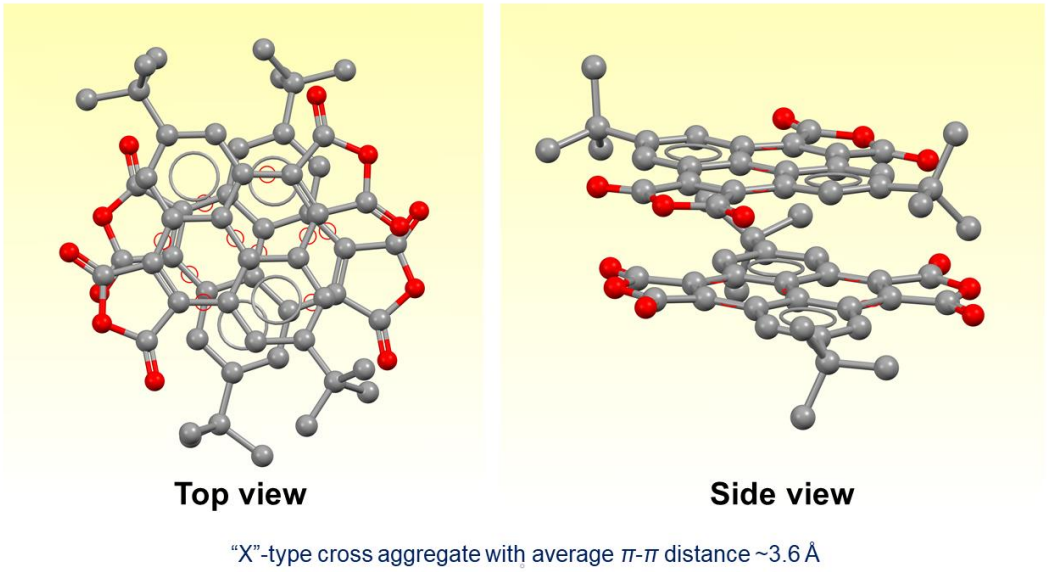


Fig. S57 Representation of top and side view of optimized geometry (ball-and-stick model) of **Py-DA** dimer obtained from DFT; H-atoms have been removed to get the better clarity of images, here grey and red-colored atoms denote C and O respectively. Also, the red-colored small circles present in the bond indicate the π-conjugation.

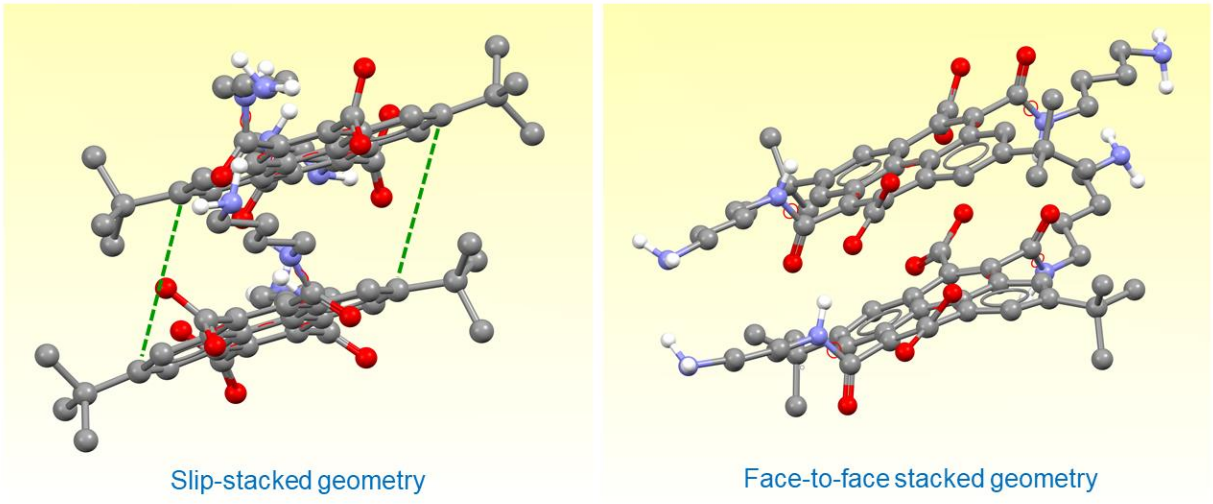


Fig. S58 Side view of **Py-1,4-DAB** symmetric dimer (left) and asymmetric dimer (right) in ball-and-stick model optimized by DFT, here white, grey, blue and red-colored atoms denote H, C, N and O respectively.

A brief discussion about the optimized molecular geometries:

*The computational study revealed that two monomers in **Py-DA** dimer preferred to exist in cross-orientation (X-cross dimer) where the average distance between two monomers is ~3.5 Å. On the other hand, in the case of symmetric **Py-1,4-DAB** dimer, the suitable orientation of two monomers was found as slip-stacked geometry with little displacement to favour the H-bonding interaction having an average distance ~4.1 Å between pyrene units. But its asymmetric version showed a different*

orientation i.e., face-to-face stacked geometry with an average distance ~3.8 Å. Also, it was found for asymmetric dimer that the below pyrene core was twisted maybe because of some extent of steric repulsion between bulky tert-butyl groups in this orientation. The symmetric ***Py-Spermidine*** *dimer also exhibited slip-stacked orientation with an average distance ~4.0 Å between pyrene units.*

Table S9. Transition characteristics of **Py-DA** and **Py-1,4-DAB** molecules.

System	Absorption maximum (nm)	Transition characteristics (% contribution)
Py-DA	**384**	H→L (95) H-1→L+2 (3)
	360	H-1→L (87) H→L+2 (11)
Py-1,4-DAB	**329**	H→L (90) H-1→L+2 (6)
	260	H→L+2 (65) H-1→L (30)

Note: *The monomer and their corresponding dimer species have almost similar transitions involved between the frontier molecular orbitals. This suggests that no charge transfer interaction (band bending) is present to stabilize the dimers rather than π-π stacking and more importantly, H-bonding interaction. Here, the ligand (diamine) has not a significant role to infer charge-transfer characteristics in the dimer. Here, H and L denote HOMO and LUMO.*

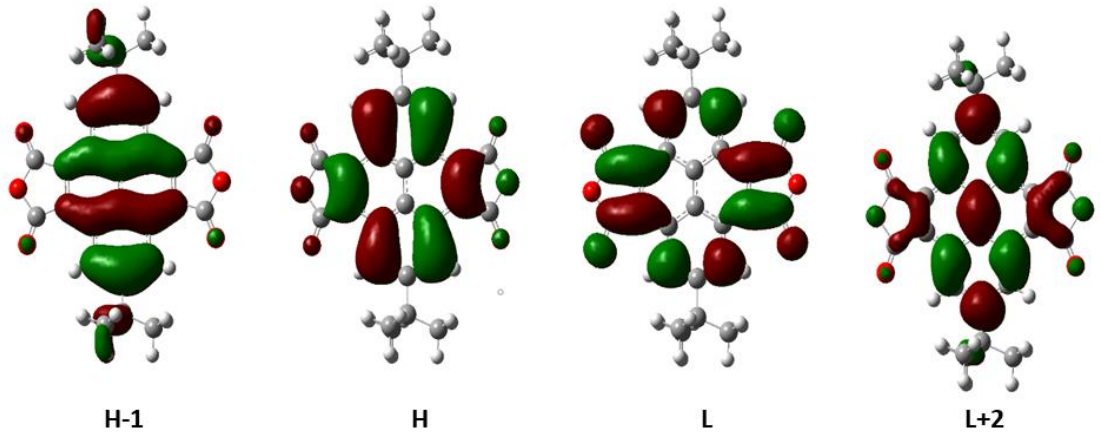


Fig. S59 Isosurface plots of some frontier molecular orbitals of **Py-DA**. H – HOMO and L – LUMO.

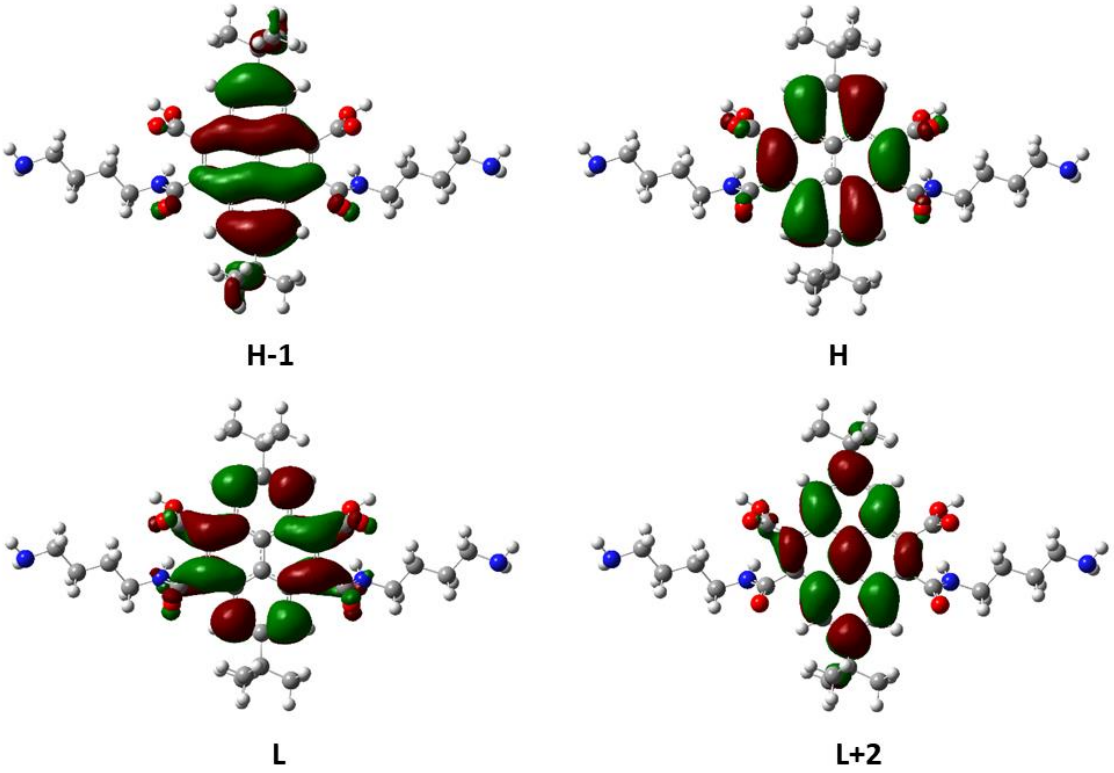


Fig. S60 Isosurface plots of some frontier molecular orbitals of **Py-1,4-DAB** species (symmetric). H – HOMO and L – LUMO.

Cartesian coordinates of the optimized geometries of different systems studied here, using B3LYP-D3/6-311G level of theory**

Py-DA

0 1 (Charge, Spin multiplicity, respectively)

C	-3.57460000	0.02240000	0.00000000
C	-2.85900000	1.22010000	0.00000000
C	-1.45540000	1.24100000	0.00000000
C	-0.71620000	0.02070000	0.00000000
C	-1.45580000	-1.20260000	0.00000000
C	-2.85270000	-1.17900000	0.00000000
C	-0.68230000	2.44020000	0.00000000
C	0.71620000	0.02070000	0.00000000
C	1.45540000	1.24100000	0.00000000
C	0.68230000	2.44020000	0.00000000
C	2.85900000	1.22010000	0.00000000
H	3.36960000	2.17140000	0.00000000

C	3.57460000	0.02240000	0.00000000
C	2.85270000	-1.17900000	0.00000000
C	1.45580000	-1.20260000	0.00000000
C	0.68130000	-2.40370000	0.00000000
C	-0.68130000	-2.40370000	0.00000000
H	-3.36960000	2.17140000	0.00000000
H	-3.37030000	-2.12850000	0.00000000
H	3.37030000	-2.12850000	0.00000000
C	5.10970000	-0.02310000	0.00000000
C	5.73440000	1.38280000	0.00000000
H	5.44890000	1.95570000	0.88620000
H	6.82360000	1.29670000	0.00000000
H	5.44890000	1.95570000	-0.88620000
C	5.59270000	-0.77320000	-1.26270000
H	5.22260000	-1.80030000	-1.29420000
H	5.25670000	-0.26410000	-2.17000000
H	6.68540000	-0.81260000	-1.27870000
C	5.59270000	-0.77320000	1.26270000
H	6.68540000	-0.81250000	1.27870000
H	5.25670000	-0.26410000	2.17000000
H	5.22260000	-1.80020000	1.29430000
C	-5.10970000	-0.02310000	0.00000000
C	-5.59270000	-0.77320000	-1.26270000
H	-5.22260000	-1.80020000	-1.29430000
H	-6.68550000	-0.81250000	-1.27870000
H	-5.25670000	-0.26400000	-2.17000000
C	-5.73440000	1.38280000	0.00000000
H	-5.44890000	1.95560000	0.88630000
H	-5.44880000	1.95570000	-0.88610000
H	-6.82360000	1.29670000	0.00000000
C	-5.59270000	-0.77320000	1.26270000
H	-5.25670000	-0.26420000	2.17000000

H	-6.68540000	-0.81260000	1.27870000
H	-5.22260000	-1.80030000	1.29420000
C	1.13900000	3.85200000	0.00000000
O	2.23890000	4.31490000	0.00000000
O	0.00000000	4.65810000	0.00000000
C	-1.13900000	3.85200000	0.00000000
O	-2.23890000	4.31490000	0.00000000
C	-1.13860000	-3.81530000	0.00000000
O	-2.23900000	-4.27690000	-0.00010000
C	1.13860000	-3.81530000	0.00000000
O	2.23900000	-4.27690000	-0.00010000
O	0.00000000	-4.62200000	0.00000000

Py-DA dimer

0 1

C	3.30550000	-0.43890000	-2.04010000
C	2.18100000	-1.27050000	-2.11240000
C	0.88630000	-0.77990000	-1.92160000
C	0.67560000	0.60350000	-1.63170000
C	1.82760000	1.43370000	-1.49730000
C	3.10840000	0.90290000	-1.70930000
C	-0.29080000	-1.57900000	-2.03320000
C	-0.64510000	1.13930000	-1.49760000
C	-1.80050000	0.31800000	-1.67690000
C	-1.54980000	-1.06440000	-1.93260000
C	-3.08040000	0.87140000	-1.57280000
H	-3.92340000	0.21480000	-1.73080000
C	-3.28280000	2.22470000	-1.27720000
C	-2.15600000	3.02980000	-1.08520000

C	-0.85520000	2.51940000	-1.19860000
C	0.32140000	3.31000000	-1.03210000
C	1.57870000	2.80110000	-1.17280000
H	2.29260000	-2.32110000	-2.34250000
H	3.94400000	1.58070000	-1.62760000
H	-2.26050000	4.07680000	-0.84340000
C	-4.70460000	2.80610000	-1.24980000
C	-5.68420000	1.84460000	-0.54300000
H	-5.37340000	1.66240000	0.48630000
H	-6.68130000	2.29200000	-0.52330000
H	-5.77270000	0.88560000	-1.05640000
C	-5.15140000	2.99850000	-2.71860000
H	-4.48200000	3.68410000	-3.24520000
H	-5.15700000	2.04760000	-3.25830000
H	-6.16230000	3.41460000	-2.75150000
C	-4.75620000	4.16370000	-0.52350000
H	-5.79050000	4.51370000	-0.48600000
H	-4.39200000	4.07920000	0.50260000
H	-4.17590000	4.93190000	-1.04020000
C	4.69080000	-1.01050000	-2.37720000
C	4.69290000	-1.41590000	-3.87040000
H	4.48660000	-0.55360000	-4.51020000
H	5.67050000	-1.82090000	-4.14640000
H	3.94210000	-2.18130000	-4.08010000
C	4.97860000	-2.25420000	-1.51050000
H	4.96520000	-2.01240000	-0.44740000
H	4.25290000	-3.05270000	-1.67190000
H	5.96540000	-2.65690000	-1.75350000
C	5.81450000	0.01540000	-2.14970000
H	5.85530000	0.35030000	-1.11050000
H	6.77770000	-0.44230000	-2.38640000
H	5.70380000	0.89530000	-2.78870000

C	-2.50930000	-2.17580000	-2.12900000
O	-3.70320000	-2.18090000	-2.17060000
O	-1.76900000	-3.34830000	-2.27750000
C	-0.40880000	-3.04370000	-2.21540000
O	0.43190000	-3.88950000	-2.27460000
C	2.54300000	3.90720000	-0.95020000
O	3.73740000	3.91030000	-0.97700000
C	0.44380000	4.75900000	-0.72880000
O	-0.39190000	5.59150000	-0.56350000
O	1.80850000	5.05580000	-0.68070000
C	3.29440000	0.43050000	2.04640000
C	2.17180000	1.26470000	2.11800000
C	0.87610000	0.77730000	1.92500000
C	0.66260000	-0.60550000	1.63430000
C	1.81270000	-1.43820000	1.50060000
C	3.09460000	-0.91060000	1.71400000
C	-0.29900000	1.57930000	2.03480000
C	-0.65920000	-1.13810000	1.49820000
C	-1.81290000	-0.31380000	1.67560000
C	-1.55920000	1.06790000	1.93190000
C	-3.09400000	-0.86390000	1.56850000
H	-3.93560000	-0.20520000	1.72490000
C	-3.29920000	-2.21650000	1.27160000
C	-2.17410000	-3.02460000	1.08240000
C	-0.87230000	-2.51760000	1.19880000
C	0.30260000	-3.31090000	1.03360000
C	1.56100000	-2.80500000	1.17530000
H	2.28550000	2.31480000	2.34900000
H	3.92870000	-1.59010000	1.63220000
H	-2.28070000	-4.07130000	0.84000000
C	-4.72260000	-2.79350000	1.23860000
C	-5.69590000	-1.82980000	0.52610000

H	-5.37970000	-1.64990000	-0.50200000
H	-6.69430000	-2.27390000	0.50240000
H	-5.78340000	-0.86980000	1.03790000
C	-5.17680000	-2.98310000	2.70540000
H	-4.51200000	-3.67020000	3.23580000
H	-5.18200000	-2.03170000	3.24420000
H	-6.18920000	-3.39620000	2.73400000
C	-4.77510000	-4.15170000	0.51330000
H	-5.81030000	-4.49860000	0.47130000
H	-4.40590000	-4.06900000	-0.51120000
H	-4.19940000	-4.92110000	1.03320000
C	4.68050000	0.99840000	2.38600000
C	4.68200000	1.40120000	3.87990000
H	4.47340000	0.53820000	4.51800000
H	5.66010000	1.80380000	4.15750000
H	3.93250000	2.16770000	4.09020000
C	4.97190000	2.24300000	1.52170000
H	4.95800000	2.00320000	0.45820000
H	4.24830000	3.04320000	1.68460000
H	5.95960000	2.64270000	1.76560000
C	5.80220000	-0.02950000	2.15760000
H	5.84260000	-0.36270000	1.11780000
H	6.76630000	0.42580000	2.39560000
H	5.68910000	-0.91020000	2.79510000
C	-2.51610000	2.18170000	2.12640000
O	-3.71010000	2.19000000	2.16550000
O	-1.77310000	3.35240000	2.27670000
C	-0.41370000	3.04430000	2.21690000
O	0.42920000	3.88800000	2.27770000
C	2.52290000	-3.91290000	0.95190000
O	3.71740000	-3.91820000	0.97770000
C	0.42210000	-4.76020000	0.73020000

O	-0.41540000	-5.59090000	0.56450000
O	1.78610000	-5.05990000	0.68240000

Py-1,4-DAB (symmetric)

0 1

C	0.01000000	3.65710000	0.19880000
C	-1.18750000	2.94430000	0.18350000
C	-1.21870000	1.54200000	0.15930000
C	0.00310000	0.81540000	0.15850000
C	1.23210000	1.53480000	0.16260000
C	1.20550000	2.93280000	0.18760000
C	-2.45300000	0.79480000	0.14790000
C	-0.00080000	-0.60630000	0.16510000
C	-1.23280000	-1.32330000	0.17160000
C	-2.46750000	-0.57320000	0.14200000
C	-1.20570000	-2.72190000	0.19450000
H	-2.14740000	-3.24880000	0.23630000
C	-0.00830000	-3.44270000	0.21270000
C	1.19170000	-2.73390000	0.19820000
C	1.22380000	-1.33100000	0.17570000
C	2.46360000	-0.58980000	0.14900000
C	2.46090000	0.77830000	0.15320000
H	-2.12570000	3.47780000	0.17720000
H	2.14510000	3.46820000	0.18610000
H	2.13180000	-3.25960000	0.24180000
C	-3.75170000	1.54720000	0.22210000
O	-4.48630000	1.57990000	1.17170000
O	-4.02240000	2.21030000	-0.93680000
H	-4.86230000	2.67550000	-0.79760000
C	3.76570000	1.51950000	0.22560000
O	4.50750000	1.53760000	1.17000000
O	4.03440000	2.19080000	-0.92930000

H	4.88070000	2.64470000	-0.79230000
C	-3.78680000	-1.31290000	0.12150000
O	-4.08340000	-2.14520000	0.96230000
C	3.77870000	-1.33770000	0.13190000
O	4.07400000	-2.16100000	0.98130000
N	-4.59510000	-0.97730000	-0.92630000
H	-4.27150000	-0.27700000	-1.57620000
N	4.58420000	-1.01810000	-0.92310000
H	4.26270000	-0.32070000	-1.57720000
C	-5.98990000	-1.39520000	-1.00100000
H	-6.21200000	-1.70870000	-2.02600000
H	-6.09170000	-2.26720000	-0.35400000
C	-6.94890000	-0.28620000	-0.55430000
H	-6.66940000	0.02820000	0.45620000
H	-6.81020000	0.58930000	-1.20290000
C	-8.41240000	-0.72980000	-0.58810000
H	-8.67730000	-1.04990000	-1.60540000
H	-8.55790000	-1.60070000	0.05910000
C	-9.37780000	0.36860000	-0.14330000
H	-9.13120000	0.66260000	0.88250000
H	-9.21960000	1.26180000	-0.77350000
C	5.97600000	-1.44590000	-0.99890000
H	6.19380000	-1.76440000	-2.02330000
H	6.07270000	-2.31650000	-0.34920000
C	6.94380000	-0.34260000	-0.55730000
H	6.66800000	-0.02270000	0.45240000
H	6.81080000	0.53170000	-1.20890000
C	8.40390000	-0.79740000	-0.59150000
H	8.66510000	-1.12290000	-1.60800000
H	8.54360000	-1.66720000	0.05850000
C	9.37820000	0.29510000	-0.15150000
H	9.22610000	1.18730000	-0.78460000

H	9.13510000	0.59440000	0.87360000
N	-10.75940000	-0.12620000	-0.15080000
H	-11.38930000	0.57850000	0.21930000
H	-11.05750000	-0.30630000	-1.10540000
N	10.75600000	-0.21030000	-0.15890000
H	11.05140000	-0.39620000	-1.11330000
H	11.39170000	0.49090000	0.20770000
C	0.05940000	5.19360000	0.22040000
C	-1.34440000	5.82430000	0.22960000
H	-1.91670000	5.55140000	-0.66140000
H	-1.91600000	5.52730000	1.11300000
H	-1.25590000	6.91350000	0.24460000
C	0.80800000	5.66180000	1.48900000
H	1.83340000	5.28670000	1.51780000
H	0.85100000	6.75450000	1.52080000
H	0.29880000	5.31240000	2.39090000
C	0.80670000	5.69610000	-1.03600000
H	1.83000000	5.31640000	-1.07920000
H	0.29270000	5.37620000	-1.94640000
H	0.85490000	6.78910000	-1.03540000
C	-0.05860000	-4.97760000	0.27680000
C	-0.85330000	-5.51640000	-0.93430000
H	-1.88100000	-5.14700000	-0.94350000
H	-0.37850000	-5.21960000	-1.87370000
H	-0.89310000	-6.60930000	-0.90190000
C	-0.76420000	-5.40050000	1.58590000
H	-0.81680000	-6.49150000	1.64990000
H	-0.21470000	-5.03280000	2.45640000
H	-1.78260000	-5.01000000	1.64320000
C	1.34430000	-5.60950000	0.25420000
H	1.88670000	-5.35880000	-0.66170000
H	1.94840000	-5.29110000	1.10750000

H	1.25480000	-6.69800000	0.29910000

Py-1,4-DAB dimer (symmetric)

0 1

C	-0.09170000	3.63480000	0.65970000
C	-1.28040000	2.91050000	0.69540000
C	-1.29780000	1.51030000	0.78540000
C	-0.07000000	0.79710000	0.85690000
C	1.15160000	1.52960000	0.82100000
C	1.11000000	2.92500000	0.73510000
C	-2.52250000	0.75120000	0.77130000
C	-0.06220000	-0.62180000	0.93630000
C	-1.28510000	-1.35210000	0.95360000
C	-2.52220000	-0.61720000	0.82940000
C	-1.24730000	-2.75210000	1.02710000
H	-2.18360000	-3.28390000	1.07990000
C	-0.04550000	-3.45970000	1.05590000
C	1.14920000	-2.73650000	1.02090000
C	1.16970000	-1.33790000	0.95750000
C	2.39890000	-0.58570000	0.85580000
C	2.38710000	0.78330000	0.82750000
H	-2.22230000	3.43250000	0.63250000
H	2.04190000	3.47000000	0.69300000
H	2.09220000	-3.25810000	1.06460000
C	-3.83100000	1.48650000	0.73620000
O	-4.62870000	1.53070000	1.63350000
O	-4.03720000	2.11130000	-0.45540000
H	-4.88530000	2.57670000	-0.38110000
C	3.69550000	1.51830000	0.84910000
O	4.49080000	1.48460000	1.74980000
O	3.91050000	2.23500000	-0.28780000
H	4.76250000	2.68490000	-0.17360000

C	-3.82350000	-1.37040000	0.70720000
O	-4.19000000	-2.19760000	1.53670000
C	3.70690000	-1.32190000	0.69300000
O	4.10460000	-2.16950000	1.48580000
N	-4.55270000	-1.07500000	-0.39970000
H	-4.19000000	-0.38970000	-1.04540000
N	4.39900000	-0.98420000	-0.42630000
H	4.00220000	-0.29130000	-1.04330000
C	-5.93890000	-1.50880000	-0.55170000
H	-6.10270000	-1.80670000	-1.59130000
H	-6.06330000	-2.39330000	0.07370000
C	-6.92990000	-0.41720000	-0.13120000
H	-6.64280000	-0.04930000	0.85810000
H	-6.84320000	0.43360000	-0.81970000
C	-8.37310000	-0.92190000	-0.09440000
H	-8.63960000	-1.37360000	-1.05950000
H	-8.46390000	-1.71210000	0.65700000
C	-9.37530000	0.18350000	0.23800000
H	-9.06640000	0.68300000	1.16150000
H	-9.35070000	0.94570000	-0.55810000
C	5.77730000	-1.40470000	-0.65630000
H	5.87530000	-1.74950000	-1.69010000
H	5.96050000	-2.25670000	-0.00100000
C	6.77430000	-0.27830000	-0.36240000
H	6.58660000	0.09770000	0.64800000
H	6.58670000	0.55670000	-1.05020000
C	8.22690000	-0.74200000	-0.48300000
H	8.39620000	-1.18960000	-1.47160000
H	8.42340000	-1.52690000	0.25320000
C	9.22880000	0.39210000	-0.26720000
H	9.08520000	1.15510000	-1.04990000
H	9.01940000	0.88010000	0.68990000

N	-10.71030000	-0.38260000	0.46740000
H	-11.36660000	0.34140000	0.74160000
H	-11.07070000	-0.80580000	-0.38260000
N	10.59850000	-0.13330000	-0.20560000
H	10.86400000	-0.54380000	-1.09590000
H	11.26110000	0.61060000	-0.01140000
C	-0.06090000	5.16230000	0.48630000
C	-1.46940000	5.78130000	0.52840000
H	-2.10030000	5.41490000	-0.28610000
H	-1.97110000	5.57440000	1.47750000
H	-1.39490000	6.86630000	0.42190000
C	0.77890000	5.81060000	1.60810000
H	1.80720000	5.44380000	1.61890000
H	0.81540000	6.89460000	1.46710000
H	0.34310000	5.60570000	2.58660000
C	0.57590000	5.48480000	-0.88550000
H	1.59670000	5.10130000	-0.95450000
H	-0.00490000	5.03940000	-1.69780000
H	0.61060000	6.56720000	-1.04150000
C	-0.02870000	-4.99610000	1.02610000
C	0.08860000	-5.43030000	-0.45410000
H	-0.75660000	-5.05790000	-1.04000000
H	1.00860000	-5.04590000	-0.90340000
H	0.10220000	-6.52210000	-0.52820000
C	-1.32110000	-5.58820000	1.62180000
H	-1.24160000	-6.67730000	1.65620000
H	-1.49940000	-5.22630000	2.63530000
H	-2.20020000	-5.34920000	1.01850000
C	1.17360000	-5.55730000	1.81110000
H	2.13160000	-5.27660000	1.36890000
H	1.16810000	-5.21120000	2.84360000
H	1.12970000	-6.64990000	1.81570000

C	0.20710000	-5.66200000	5.48910000
C	1.40920000	-4.96550000	5.38950000
C	1.45160000	-3.57680000	5.18690000
C	0.23250000	-2.85010000	5.11150000
C	-1.00240000	-3.55640000	5.16950000
C	-0.98410000	-4.94200000	5.35920000
C	2.69210000	-2.84120000	5.10480000
C	0.24410000	-1.43150000	5.02140000
C	1.47790000	-0.72440000	5.00770000
C	2.70940000	-1.47410000	5.04230000
C	1.46400000	0.67650000	4.96800000
H	2.41260000	1.18880000	4.99430000
C	0.27360000	1.40320000	4.96480000
C	-0.93310000	0.69970000	4.97560000
C	-0.97640000	-0.69970000	5.00880000
C	-2.22350000	-1.42810000	5.04260000
C	-2.22910000	-2.79500000	5.09530000
H	2.34320000	-5.50060000	5.45890000
H	-1.92620000	-5.46920000	5.41620000
H	-1.86980000	1.23290000	5.01530000
C	3.99180000	-3.59130000	5.13240000
O	4.85790000	-3.47890000	5.95940000
O	4.09660000	-4.44530000	4.07910000
H	4.96530000	-4.86760000	4.15690000
C	-3.53690000	-3.53070000	5.14030000
O	-4.36960000	-3.44800000	6.00380000
O	-3.68620000	-4.33810000	4.05620000
H	-4.56200000	-4.74600000	4.13320000
C	4.02480000	-0.72030000	5.04990000
O	4.29990000	0.07230000	5.93930000
C	-3.52780000	-0.65670000	5.09620000
O	-3.74730000	0.14970000	5.98940000

N	4.82010000	-1.01860000	4.00060000
H	4.44330000	-1.58470000	3.24850000
N	-4.38490000	-0.95660000	4.09680000
H	-4.07930000	-1.56070000	3.34210000
C	6.17900000	-0.52810000	3.85460000
H	6.20830000	0.24240000	3.07590000
H	6.45430000	-0.05140000	4.79650000
C	7.13350000	-1.67530000	3.51340000
H	7.11940000	-2.39790000	4.33680000
H	6.74780000	-2.19990000	2.62940000
C	8.56070000	-1.19580000	3.24820000
H	8.54890000	-0.45650000	2.43810000
H	8.96210000	-0.67790000	4.12520000
C	9.51780000	-2.32730000	2.86970000
H	9.61490000	-3.00620000	3.72450000
H	9.05790000	-2.92140000	2.05700000
C	-5.76770000	-0.50600000	4.05880000
H	-5.89040000	0.22390000	3.25290000
H	-5.96540000	0.00750000	5.00070000
C	-6.71850000	-1.69090000	3.86150000
H	-6.61210000	-2.37120000	4.71350000
H	-6.40000000	-2.24640000	2.97070000
C	-8.17590000	-1.25560000	3.70390000
H	-8.25610000	-0.56000000	2.85940000
H	-8.51180000	-0.70240000	4.58690000
C	-9.13150000	-2.42720000	3.47170000
H	-8.74070000	-3.04000000	2.63690000
H	-9.11460000	-3.07330000	4.35670000
N	10.84330000	-1.79810000	2.53870000
H	11.50340000	-2.56180000	2.43030000
H	10.80720000	-1.31370000	1.64020000
N	-10.50250000	-1.95240000	3.26710000

H	-10.58800000	-1.51010000	2.35050000
H	-11.14440000	-2.73890000	3.26870000
C	0.14830000	-7.17720000	5.74580000
C	1.54790000	-7.81400000	5.81010000
H	2.09790000	-7.67350000	4.87540000
H	2.14450000	-7.40000000	6.62710000
H	1.45340000	-8.88930000	5.98250000
C	-0.56340000	-7.42910000	7.09460000
H	-1.58410000	-7.04000000	7.09120000
H	-0.61300000	-8.50230000	7.30330000
H	-0.02420000	-6.94460000	7.91270000
C	-0.64020000	-7.86920000	4.61150000
H	-1.65710000	-7.48120000	4.52380000
H	-0.14350000	-7.72070000	3.65030000
H	-0.70720000	-8.94470000	4.80130000
C	0.28880000	2.93480000	5.08790000
C	1.56820000	3.53870000	4.47460000
H	2.46690000	3.23220000	5.01280000
H	1.67990000	3.24490000	3.42830000
H	1.52100000	4.62980000	4.52070000
C	0.24390000	3.27970000	6.59500000
H	0.25330000	4.36520000	6.73890000
H	-0.66130000	2.87830000	7.05750000
H	1.10650000	2.85540000	7.11500000
C	-0.93310000	3.56870000	4.39290000
H	-0.97790000	3.28410000	3.34030000
H	-1.87320000	3.27810000	4.86520000
H	-0.86800000	4.65910000	4.45340000

Py-1,4-DAB (asymmetric)

0 1

C	-0.10100000	3.70520000	-0.22230000

C	-1.27310000	2.96790000	-0.06720000
C	-1.27640000	1.56530000	-0.08770000
C	-0.05050000	0.86580000	-0.25940000
C	1.15410000	1.61110000	-0.41730000
C	1.09880000	3.00920000	-0.39420000
C	-2.48530000	0.79360000	0.06880000
C	-0.03070000	-0.55610000	-0.26630000
C	-1.23570000	-1.29890000	-0.09830000
C	-2.47650000	-0.57420000	0.05350000
C	-1.18000000	-2.69670000	-0.09990000
H	-2.09700000	-3.24290000	0.06320000
C	0.02050000	-3.39410000	-0.26010000
C	1.19290000	-2.66020000	-0.43050000
C	1.19530000	-1.25700000	-0.43570000
C	2.40180000	-0.48250000	-0.61290000
C	2.39330000	0.88690000	-0.58460000
H	-2.21490000	3.48110000	0.05510000
H	2.01590000	3.55790000	-0.54680000
H	2.13570000	-3.17400000	-0.53480000
C	-3.77420000	1.52100000	0.33240000
O	-4.36030000	1.54310000	1.38050000
O	-4.22550000	2.17320000	-0.77450000
H	-5.04410000	2.62420000	-0.51460000
C	-3.77000000	-1.34020000	0.21680000
O	-3.92440000	-2.18560000	1.08280000
C	3.69450000	-1.21670000	-0.82270000
O	4.20070000	-1.97380000	-0.02920000
N	-4.72940000	-1.01180000	-0.69690000
H	-4.51550000	-0.30390000	-1.38300000
C	-6.11340000	-1.45200000	-0.57030000
H	-6.47300000	-1.78230000	-1.55010000
H	-6.10810000	-2.31710000	0.09380000

C	-7.01800000	-0.35130000	-0.00520000
H	-6.60360000	-0.01820000	0.95170000
H	-6.98770000	0.51670000	-0.67750000
C	-8.46400000	-0.81720000	0.17410000
H	-8.86430000	-1.15660000	-0.79120000
H	-8.50180000	-1.68030000	0.84660000
C	-9.37530000	0.27330000	0.73680000
H	-8.99110000	0.58700000	1.71330000
H	-9.32320000	1.15880000	0.07860000
N	-10.73540000	-0.24230000	0.93180000
H	-11.31880000	0.45910000	1.37680000
H	-11.16200000	-0.44250000	0.03140000
C	-0.08240000	5.24220000	-0.22920000
C	-1.48160000	5.84590000	-0.01500000
H	-2.17590000	5.54990000	-0.80640000
H	-1.90760000	5.55090000	0.94810000
H	-1.41480000	6.93670000	-0.02650000
C	0.84130000	5.74680000	0.90270000
H	1.86690000	5.39400000	0.77520000
H	0.86350000	6.84060000	0.91200000
H	0.48460000	5.40320000	1.87740000
C	0.45670000	5.73340000	-1.59240000
H	1.46690000	5.36700000	-1.78600000
H	-0.18540000	5.39070000	-2.40830000
H	0.48470000	6.82710000	-1.61480000
C	0.00450000	-4.93060000	-0.21760000
C	-0.93400000	-5.46380000	-1.32390000
H	-1.95910000	-5.11180000	-1.19100000
H	-0.59170000	-5.14300000	-2.31160000
H	-0.95270000	-6.55760000	-1.30680000
C	-0.51580000	-5.38840000	1.16460000
H	-0.54310000	-6.48120000	1.21390000

H	0.13770000	-5.02610000	1.96260000
H	-1.52340000	-5.01700000	1.36300000
C	1.40160000	-5.53730000	-0.43600000
H	1.81390000	-5.26410000	-1.41140000
H	2.10770000	-5.22210000	0.33680000
H	1.33590000	-6.62770000	-0.39850000
C	3.68580000	1.66060000	-0.72040000
O	3.85010000	2.53130000	-1.56030000
N	4.63960000	1.31750000	0.19230000
H	4.43940000	0.58190000	0.85240000
C	6.00720000	1.81450000	0.09690000
H	6.42660000	1.85780000	1.10580000
H	5.95760000	2.83270000	-0.29280000
C	6.88190000	0.94830000	-0.81700000
H	6.42120000	0.93330000	-1.81020000
H	6.87640000	-0.08260000	-0.44080000
C	8.31840000	1.46470000	-0.91450000
H	8.76940000	1.48570000	0.08700000
H	8.32670000	2.49630000	-1.28110000
C	9.19400000	0.61740000	-1.83760000
H	9.16940000	-0.43100000	-1.49170000
H	8.75990000	0.62620000	-2.84350000
N	10.54550000	1.18210000	-1.92670000
H	11.01620000	1.09420000	-1.03050000
H	11.10280000	0.66080000	-2.59610000
O	4.24310000	-0.93800000	-2.02270000
H	5.09690000	-1.39640000	-2.05750000

Py-1,4-DAB dimer (asymmetric)

0 1

C	0.34480000	3.57450000	0.48620000
C	-0.71740000	2.78030000	0.90930000

C	-0.70900000	1.38320000	0.76960000
C	0.46770000	0.75250000	0.28120000
C	1.54920000	1.55910000	-0.17150000
C	1.45560000	2.94760000	-0.08090000
C	-1.83870000	0.54180000	1.10970000
C	0.57740000	-0.66330000	0.25390000
C	-0.50120000	-1.47530000	0.70260000
C	-1.72890000	-0.82940000	1.09040000
C	-0.36400000	-2.87500000	0.69670000
H	-1.18460000	-3.46780000	1.07110000
C	0.79820000	-3.49120000	0.24210000
C	1.84840000	-2.67960000	-0.20340000
C	1.77440000	-1.28630000	-0.20490000
C	2.86080000	-0.44080000	-0.65810000
C	2.74300000	0.92060000	-0.65800000
H	-1.57890000	3.24610000	1.35540000
H	2.27860000	3.54120000	-0.45380000
H	2.76050000	-3.14840000	-0.54260000
C	-3.17290000	1.13090000	1.42130000
O	-3.95840000	0.70560000	2.24120000
O	-3.49540000	2.18920000	0.64750000
H	-4.36160000	2.49480000	0.95660000
C	-2.91960000	-1.71400000	1.40100000
O	-3.00110000	-2.35490000	2.43600000
C	4.17920000	-1.05840000	-0.99320000
O	4.77800000	-1.85360000	-0.28830000
N	-3.84500000	-1.76540000	0.40390000
H	-3.70220000	-1.16900000	-0.39720000
C	-5.15710000	-2.37860000	0.58290000
H	-5.38380000	-2.99900000	-0.29000000
H	-5.07710000	-3.03780000	1.44810000
C	-6.25480000	-1.33160000	0.80050000

H	-5.97320000	-0.70090000	1.64820000
H	-6.29540000	-0.67170000	-0.07640000
C	-7.63290000	-1.95140000	1.04400000
H	-7.88150000	-2.64290000	0.22760000
H	-7.61820000	-2.54550000	1.96310000
C	-8.72710000	-0.89030000	1.15530000
H	-8.45880000	-0.18580000	1.94780000
H	-8.75800000	-0.31570000	0.21460000
N	-10.02040000	-1.49050000	1.51260000
H	-10.73900000	-0.77360000	1.53910000
H	-10.30490000	-2.15860000	0.80160000
C	0.33720000	5.10230000	0.62340000
C	-0.92790000	5.61160000	1.33630000
H	-1.82950000	5.38250000	0.76100000
H	-1.03730000	5.17740000	2.33270000
H	-0.87480000	6.69770000	1.44770000
C	1.57690000	5.52470000	1.44250000
H	2.50670000	5.27460000	0.92790000
H	1.57110000	6.60480000	1.61710000
H	1.58550000	5.01110000	2.40450000
C	0.40010000	5.74270000	-0.78100000
H	1.29680000	5.43850000	-1.32550000
H	-0.46930000	5.45460000	-1.37830000
H	0.41210000	6.83370000	-0.69710000
C	0.98200000	-5.01620000	0.20830000
C	1.22550000	-5.46670000	-1.25050000
H	0.37430000	-5.20610000	-1.88560000
H	2.11780000	-5.00300000	-1.67690000
H	1.36280000	-6.55140000	-1.29030000
C	-0.25360000	-5.76370000	0.73610000
H	-0.07540000	-6.84120000	0.69630000
H	-0.47510000	-5.50570000	1.77200000

H	-1.14170000	-5.55220000	0.13390000
C	2.20590000	-5.39550000	1.07440000
H	3.13190000	-4.98260000	0.66840000
H	2.10620000	-5.01460000	2.09200000
H	2.31470000	-6.48320000	1.11660000
C	3.91090000	1.80130000	-1.06140000
O	3.96320000	2.37560000	-2.13580000
N	4.86580000	1.85020000	-0.10100000
H	4.57670000	1.63890000	0.85010000
C	6.10480000	2.59530000	-0.28120000
H	6.47520000	2.84400000	0.71640000
H	5.89900000	3.53040000	-0.80990000
C	7.14950000	1.77490000	-1.04700000
H	6.83730000	1.70240000	-2.09410000
H	7.13870000	0.75570000	-0.64290000
C	8.55970000	2.35100000	-0.93240000
H	8.83970000	2.40150000	0.12620000
H	8.59580000	3.37650000	-1.31440000
C	9.61470000	1.51280000	-1.65520000
H	9.44430000	0.44840000	-1.41010000
H	9.48090000	1.60850000	-2.73860000
N	10.95620000	1.98600000	-1.30160000
H	11.11410000	1.76560000	-0.32040000
H	11.66030000	1.48750000	-1.83700000
O	4.67480000	-0.64890000	-2.16610000
H	5.57150000	-1.00970000	-2.24460000
C	0.74930000	3.84830000	4.97490000
C	-0.56980000	3.38490000	5.07570000
C	-0.91950000	2.05130000	4.84750000
C	0.11570000	1.12840000	4.51970000
C	1.42520000	1.61410000	4.25770000
C	1.71810000	2.96850000	4.50140000

C	-2.26320000	1.53200000	5.06280000
C	-0.13050000	-0.27040000	4.54090000
C	-1.38650000	-0.74930000	5.00590000
C	-2.45730000	0.18730000	5.23520000
C	-1.57640000	-2.11880000	5.17620000
H	-2.52500000	-2.45990000	5.56280000
C	-0.58230000	-3.04640000	4.86720000
C	0.62060000	-2.57870000	4.34310000
C	0.88390000	-1.20370000	4.18690000
C	2.15250000	-0.67500000	3.71910000
C	2.42000000	0.67420000	3.80900000
H	-1.34150000	4.06860000	5.39550000
H	2.72530000	3.31460000	4.32860000
H	1.40420000	-3.27120000	4.09110000
C	-3.46290000	2.41140000	5.04200000
O	-4.50360000	2.21980000	5.61890000
O	-3.31150000	3.48810000	4.20730000
H	-4.14760000	3.97330000	4.26620000
C	-3.77580000	-0.42780000	5.67730000
O	-3.96070000	-0.68790000	6.85600000
C	3.14010000	-1.59740000	3.06060000
O	3.31670000	-2.76680000	3.31990000
N	-4.59330000	-0.75830000	4.66050000
H	-4.30730000	-0.49560000	3.72790000
C	-5.88860000	-1.38250000	4.84980000
H	-6.00760000	-2.15650000	4.08340000
H	-5.87780000	-1.87540000	5.82370000
C	-7.04880000	-0.38380000	4.77780000
H	-6.93920000	0.33810000	5.59300000
H	-6.96280000	0.18990000	3.84630000
C	-8.40470000	-1.08730000	4.83980000
H	-8.48360000	-1.79930000	4.00920000

H	-8.48680000	-1.67660000	5.75920000
C	-9.59990000	-0.13880000	4.76240000
H	-9.62770000	0.48780000	5.66080000
H	-9.45430000	0.54840000	3.90890000
N	-10.84380000	-0.91330000	4.69060000
H	-11.64800000	-0.29480000	4.65460000
H	-10.83630000	-1.45340000	3.82820000
C	1.09610000	5.25300000	5.50430000
C	0.18460000	6.33560000	4.88840000
H	0.34550000	6.42340000	3.81460000
H	-0.87410000	6.12600000	5.05440000
H	0.40280000	7.30610000	5.34370000
C	0.88180000	5.23250000	7.03780000
H	1.50590000	4.46710000	7.50640000
H	1.14440000	6.20300000	7.47020000
H	-0.15850000	5.01830000	7.29350000
C	2.56160000	5.63980000	5.23310000
H	3.25720000	4.96150000	5.73400000
H	2.79530000	5.64330000	4.16640000
H	2.75020000	6.64530000	5.61820000
C	-0.85900000	-4.53470000	5.12680000
C	-2.09870000	-4.96940000	4.31190000
H	-2.99470000	-4.42920000	4.62180000
H	-1.96240000	-4.76520000	3.24910000
H	-2.28160000	-6.03980000	4.44760000
C	-1.14110000	-4.73840000	6.63360000
H	-1.35030000	-5.79310000	6.83750000
H	-0.27740000	-4.43860000	7.23350000
H	-2.00110000	-4.15530000	6.96970000
C	0.33180000	-5.42650000	4.73960000
H	0.57790000	-5.33970000	3.68060000
H	1.22750000	-5.17820000	5.31520000

H	0.08720000	-6.47330000	4.93780000
C	3.78220000	1.22990000	3.47200000
O	3.95470000	2.06590000	2.58810000
N	4.78770000	0.79330000	4.26780000
H	4.57880000	0.07460000	4.94360000
C	6.18100000	1.13650000	4.00410000
H	6.72260000	1.10450000	4.95320000
H	6.19710000	2.16790000	3.64640000
C	6.84540000	0.21490000	2.97370000
H	6.25740000	0.23530000	2.05180000
H	6.81180000	-0.81770000	3.34020000
C	8.29070000	0.62860000	2.68440000
H	8.85950000	0.66540000	3.62360000
H	8.31400000	1.64130000	2.26910000
C	8.99520000	-0.31790000	1.71370000
H	8.98100000	-1.33600000	2.13480000
H	8.43040000	-0.35800000	0.77790000
N	10.34960000	0.16350000	1.39950000
H	10.92280000	0.15950000	2.23890000
H	10.79850000	-0.46730000	0.74230000
O	3.80300000	-0.97130000	2.07600000
H	4.30230000	-1.60880000	1.52530000

Py-Spermidine

0 1

C	0.00610000	2.83760000	0.25390000
C	-1.19130000	2.12810000	0.17900000
C	-1.22190000	0.73230000	0.04080000
C	0.00000000	0.00840000	-0.01770000
C	1.22860000	0.72530000	0.04710000
C	1.20180000	2.11660000	0.18570000
C	-2.45560000	-0.01160000	-0.03360000

C	-0.00340000	-1.40910000	-0.12750000
C	-1.23490000	-2.12450000	-0.18130000
C	-2.46930000	-1.37480000	-0.15210000
C	-1.20770000	-3.52030000	-0.27160000
H	-2.14950000	-4.04870000	-0.27480000
C	-0.00990000	-4.24000000	-0.30950000
C	1.18990000	-3.53210000	-0.26500000
C	1.22140000	-2.13200000	-0.17420000
C	2.46050000	-1.39080000	-0.13930000
C	2.45740000	-0.02740000	-0.02240000
H	-2.12990000	2.66010000	0.21490000
H	2.14140000	2.65040000	0.22950000
H	2.13050000	-4.05900000	-0.26300000
C	-3.75570000	0.73150000	0.10060000
O	-4.48700000	0.68790000	1.05320000
O	-4.03140000	1.47810000	-1.00280000
H	-4.87830000	1.92100000	-0.83500000
C	3.76220000	0.70620000	0.11290000
O	4.49600000	0.65290000	1.06310000
O	4.04020000	1.45740000	-0.98710000
H	4.89210000	1.89090000	-0.81990000
C	-3.79010000	-2.10780000	-0.22880000
O	-4.09180000	-2.99530000	0.55150000
C	3.77780000	-2.13140000	-0.20950000
O	4.07600000	-3.01120000	0.58020000
N	-4.59560000	-1.69220000	-1.25030000
H	-4.26640000	-0.94340000	-1.84100000
N	4.58400000	-1.72940000	-1.23610000
H	4.25820000	-0.98310000	-1.83190000
C	-6.01130000	-2.03760000	-1.31830000
H	-6.25830000	-2.34580000	-2.33940000
H	-6.15280000	-2.89920000	-0.66430000

C	-6.88870000	-0.86430000	-0.87180000
H	-6.54610000	-0.54220000	0.11430000
H	-6.75330000	-0.01580000	-1.55310000
C	-8.37690000	-1.21400000	-0.83270000
H	-8.68250000	-1.59430000	-1.81380000
H	-8.53170000	-2.03440000	-0.10730000
C	5.99760000	-2.08370000	-1.30260000
H	6.24260000	-2.39700000	-2.32260000
H	6.13360000	-2.94370000	-0.64550000
C	6.88240000	-0.91440000	-0.86000000
H	6.54200000	-0.58740000	0.12530000
H	6.75180000	-0.06720000	-1.54380000
C	8.36830000	-1.27300000	-0.82010000
H	8.67150000	-1.65810000	-1.80010000
H	8.51830000	-2.09210000	-0.09230000
C	0.05540000	4.36710000	0.40080000
C	-1.34850000	4.99500000	0.45920000
H	-1.91960000	4.79590000	-0.45190000
H	-1.92160000	4.62720000	1.31460000
H	-1.26000000	6.07930000	0.56320000
C	0.80230000	4.72980000	1.70450000
H	1.82760000	4.35340000	1.70420000
H	0.84550000	5.81630000	1.82530000
H	0.29150000	4.30830000	2.57410000
C	0.80480000	4.97000000	-0.80940000
H	1.82820000	4.59520000	-0.88170000
H	0.29220000	4.72550000	-1.74360000
H	0.85290000	6.05930000	-0.71960000
C	-0.05990000	-5.77510000	-0.36920000
C	-0.85210000	-6.21500000	-1.62130000
H	-1.87960000	-5.84540000	-1.60320000
H	-0.37510000	-5.84400000	-2.53280000

H	-0.89210000	-7.30690000	-1.67670000
C	-0.76800000	-6.30200000	0.90030000
H	-0.82070000	-7.39470000	0.87630000
H	-0.22020000	-6.00540000	1.79850000
H	-1.78650000	-5.91720000	0.98690000
C	1.34310000	-6.40320000	-0.43950000
H	1.88760000	-6.07940000	-1.33100000
H	1.94510000	-6.15450000	0.43810000
H	1.25360000	-7.49180000	-0.48270000
N	-9.19890000	-0.03970000	-0.53620000
H	-10.16440000	-0.24830000	-0.77040000
N	9.19760000	-0.10280000	-0.52730000
H	10.16180000	-0.31800000	-0.76070000
C	-9.14310000	0.40350000	0.85890000
H	-9.36300000	-0.41660000	1.56780000
H	-8.12390000	0.73560000	1.08000000
C	-10.10700000	1.56290000	1.10320000
H	-11.13360000	1.22700000	0.90200000
H	-9.89100000	2.35230000	0.37470000
C	-10.02130000	2.12260000	2.52510000
H	-10.21160000	1.31800000	3.24810000
H	-9.00890000	2.48720000	2.72820000
C	-11.00570000	3.26350000	2.77960000
H	-12.02990000	2.90470000	2.57650000
H	-10.80980000	4.06960000	2.06350000
C	9.14440000	0.34520000	0.86630000
H	9.35940000	-0.47400000	1.57790000
H	8.12720000	0.68390000	1.08640000
C	10.11510000	1.49970000	1.10690000
H	11.13970000	1.15690000	0.90730000
H	9.90400000	2.28780000	0.37560000
C	10.03220000	2.06490000	2.52680000

H	10.21720000	1.26170000	3.25270000
H	9.02200000	2.43640000	2.72820000
C	11.02350000	3.20060000	2.77770000
H	12.04560000	2.83470000	2.57680000
H	10.83320000	4.00520000	2.05840000
N	-10.82430000	3.80930000	4.13060000
H	-11.45390000	4.59110000	4.28230000
H	-11.07000000	3.10540000	4.82140000
N	10.84450000	3.75260000	4.12650000
H	11.08500000	3.04980000	4.82010000
H	11.47910000	4.53090000	4.27590000

Py-Spermidine dimer

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C	-0.44500000	3.55320000	1.96040000
C	-1.58660000	2.75400000	1.94460000
C	-1.52760000	1.35530000	1.84330000
C	-0.24710000	0.72670000	1.81540000
C	0.92730000	1.53620000	1.82000000
C	0.80020000	2.92600000	1.89950000
C	-2.70650000	0.51160000	1.73860000
C	-0.13250000	-0.68860000	1.75340000
C	-1.29810000	-1.50080000	1.75500000
C	-2.58270000	-0.85670000	1.71770000
C	-1.17370000	-2.89690000	1.67970000
H	-2.07220000	-3.49220000	1.73350000
C	0.06430000	-3.51960000	1.54130000
C	1.20750000	-2.71440000	1.53480000
C	1.14010000	-1.31950000	1.64000000
C	2.31120000	-0.47860000	1.56000000
C	2.20790000	0.88040000	1.68100000
H	-2.55290000	3.22290000	1.98750000

H	1.69330000	3.53250000	1.87980000
H	2.18130000	-3.17340000	1.45960000
C	-4.09290000	1.05470000	1.59020000
O	-5.09220000	0.50830000	1.99540000
O	-4.16580000	2.20860000	0.88210000
H	-5.10560000	2.44400000	0.85090000
C	3.47110000	1.69040000	1.67880000
O	4.36130000	1.58550000	2.47950000
O	3.52900000	2.56290000	0.63520000
H	4.36120000	3.05160000	0.73220000
C	-3.78020000	-1.76690000	1.54290000
O	-4.22970000	-2.43030000	2.46970000
C	3.63230000	-1.11190000	1.19640000
O	4.16460000	-2.00630000	1.84610000
N	-4.23020000	-1.85500000	0.27040000
H	-3.82670000	-1.22980000	-0.41050000
N	4.16580000	-0.64680000	0.03780000
H	3.67690000	0.07710000	-0.46550000
C	-5.44120000	-2.58150000	-0.09210000
H	-5.24260000	-3.14180000	-1.01190000
H	-5.62370000	-3.30420000	0.70410000
C	-6.65080000	-1.65980000	-0.27700000
H	-6.87290000	-1.16520000	0.67270000
H	-6.41270000	-0.86970000	-0.99730000
C	-7.86420000	-2.43300000	-0.80220000
H	-7.57510000	-2.93740000	-1.73110000
H	-8.13290000	-3.22990000	-0.08580000
C	5.45250000	-1.11760000	-0.46240000
H	5.43780000	-1.03260000	-1.55240000
H	5.53130000	-2.17670000	-0.20890000
C	6.64520000	-0.35760000	0.12550000
H	6.63950000	-0.46040000	1.21210000

H	6.54040000	0.71180000	-0.09630000
C	7.96490000	-0.87730000	-0.44220000
H	7.97040000	-0.73080000	-1.53910000
H	8.03310000	-1.95950000	-0.27570000
C	-0.52810000	5.08970000	1.94000000
C	-1.95090000	5.59990000	2.23330000
H	-2.66540000	5.28260000	1.46950000
H	-2.30700000	5.25340000	3.20710000
H	-1.95130000	6.69270000	2.24670000
C	0.42310000	5.71140000	2.98410000
H	1.46490000	5.42970000	2.81840000
H	0.36700000	6.80230000	2.93160000
H	0.15040000	5.40300000	3.99320000
C	-0.11400000	5.56430000	0.52690000
H	0.90740000	5.25650000	0.28860000
H	-0.77750000	5.14390000	-0.23370000
H	-0.16470000	6.65550000	0.46270000
C	0.17750000	-5.02950000	1.28090000
C	0.36360000	-5.21920000	-0.24360000
H	-0.48370000	-4.80370000	-0.79680000
H	1.27310000	-4.72250000	-0.59270000
H	0.44220000	-6.28360000	-0.48520000
C	-1.09170000	-5.78110000	1.72500000
H	-0.94610000	-6.85540000	1.58970000
H	-1.32230000	-5.59720000	2.77570000
H	-1.96380000	-5.49770000	1.12980000
C	1.39070000	-5.63590000	2.01330000
H	2.33910000	-5.21280000	1.67750000
H	1.31960000	-5.47530000	3.08720000
H	1.43050000	-6.71300000	1.82700000
C	0.28810000	-5.90020000	5.62540000
C	1.47370000	-5.17480000	5.55440000

C	1.47990000	-3.77550000	5.45600000
C	0.24410000	-3.07310000	5.46590000
C	-0.97900000	-3.80460000	5.46310000
C	-0.92070000	-5.20060000	5.55130000
C	2.70550000	-3.01290000	5.41200000
C	0.23500000	-1.65360000	5.53930000
C	1.45580000	-0.92480000	5.57440000
C	2.70140000	-1.64710000	5.48480000
C	1.41750000	0.46810000	5.72420000
H	2.35760000	0.99190000	5.78460000
C	0.21800000	1.16220000	5.87790000
C	-0.97410000	0.43810000	5.83740000
C	-0.99480000	-0.95330000	5.67360000
C	-2.23210000	-1.69840000	5.64510000
C	-2.22730000	-3.05990000	5.47650000
H	2.42090000	-5.69120000	5.57270000
H	-1.84550000	-5.75540000	5.58390000
H	-1.91420000	0.94350000	5.99170000
C	4.01500000	-3.74430000	5.34020000
O	4.88630000	-3.71870000	6.16840000
O	4.11720000	-4.46750000	4.19360000
H	4.99460000	-4.87920000	4.20680000
C	-3.54020000	-3.75670000	5.31390000
O	-4.55680000	-3.49740000	5.90730000
O	-3.50160000	-4.72110000	4.35400000
H	-4.41470000	-5.02770000	4.25380000
C	4.00170000	-0.87330000	5.55660000
O	4.25990000	-0.16070000	6.51770000
C	-3.49980000	-0.89910000	5.90520000
O	-3.66120000	-0.38340000	7.00210000
N	4.81010000	-1.05320000	4.49150000
H	4.46180000	-1.56030000	3.68530000

N	-4.31650000	-0.73900000	4.84280000
H	-4.15610000	-1.33560000	4.03820000
C	6.14980000	-0.49540000	4.41740000
H	6.14260000	0.39330000	3.77660000
H	6.41400000	-0.16940000	5.42500000
C	7.15090000	-1.52560000	3.89410000
H	7.08950000	-2.43650000	4.49610000
H	6.88050000	-1.81070000	2.87070000
C	8.58400000	-0.99330000	3.92300000
H	8.60470000	0.05130000	3.56050000
H	8.92800000	-0.96370000	4.96250000
C	-5.64660000	-0.16040000	4.97740000
H	-5.69580000	0.77410000	4.41030000
H	-5.78810000	0.07710000	6.03320000
C	-6.73010000	-1.12130000	4.48440000
H	-6.69820000	-2.04170000	5.07270000
H	-6.51590000	-1.39200000	3.44420000
C	-8.11350000	-0.48690000	4.58300000
H	-8.13140000	0.44770000	3.98920000
H	-8.30100000	-0.19290000	5.62270000
C	0.26510000	-7.42940000	5.79170000
C	1.67950000	-8.03580000	5.81380000
H	2.22050000	-7.83190000	4.88540000
H	2.27180000	-7.65370000	6.64920000
H	1.61090000	-9.12100000	5.92650000
C	-0.43310000	-7.77710000	7.12620000
H	-1.46380000	-7.41650000	7.14840000
H	-0.45290000	-8.86150000	7.27280000
H	0.09720000	-7.32640000	7.96910000
C	-0.51220000	-8.07260000	4.62200000
H	-1.53640000	-7.69940000	4.55700000
H	-0.01980000	-7.86240000	3.67020000

H	-0.55830000	-9.15810000	4.75230000
C	0.21790000	2.65720000	6.23220000
C	1.45850000	3.37310000	5.66130000
H	2.38460000	3.00800000	6.10930000
H	1.52720000	3.24080000	4.57920000
H	1.39890000	4.44390000	5.87330000
C	0.24360000	2.76610000	7.77510000
H	0.24540000	3.81670000	8.08380000
H	-0.63160000	2.27920000	8.21270000
H	1.13690000	2.28550000	8.18180000
C	-1.04640000	3.36390000	5.70290000
H	-1.14600000	3.23460000	4.62370000
H	-1.95530000	2.98870000	6.17720000
H	-0.99100000	4.43440000	5.92100000
N	9.48680000	-1.85370000	3.15890000
H	9.32630000	-1.64960000	2.17340000
N	-9.17360000	-1.41310000	4.19110000
H	-9.01340000	-1.72590000	3.23700000
N	-8.99710000	-1.55660000	-1.10220000
H	-9.52160000	-1.95020000	-1.87560000
N	9.11500000	-0.25070000	0.20190000
H	8.98060000	0.75620000	0.22950000
C	-9.92080000	-1.33650000	0.01050000
H	-10.32230000	-2.28670000	0.41050000
H	-9.37620000	-0.86310000	0.83520000
C	-11.08080000	-0.44010000	-0.42680000
H	-11.48010000	-0.82490000	-1.37520000
H	-10.69610000	0.56240000	-0.64230000
C	-12.21600000	-0.37870000	0.59580000
H	-12.60050000	-1.39220000	0.76410000
H	-11.84170000	-0.03110000	1.56240000
C	-13.37280000	0.51850000	0.15530000

H	-13.62610000	0.28970000	-0.89350000
H	-13.05030000	1.56460000	0.17840000
C	10.38670000	-0.54840000	-0.45810000
H	10.34490000	-0.36020000	-1.54680000
H	10.58380000	-1.62000000	-0.33940000
C	11.53280000	0.25500000	0.15310000
H	11.38580000	1.32010000	-0.07080000
H	11.48550000	0.15480000	1.24080000
C	12.90960000	-0.19590000	-0.33970000
H	12.94360000	-0.17170000	-1.43700000
H	13.08020000	-1.23500000	-0.04510000
C	14.04730000	0.65830000	0.21980000
H	13.96290000	1.68140000	-0.18100000
H	13.93780000	0.73740000	1.30610000
C	10.89890000	-1.61000000	3.44030000
H	11.19160000	-0.55630000	3.26540000
H	11.07640000	-1.79960000	4.50530000
C	11.79270000	-2.52870000	2.60800000
H	11.49290000	-2.45320000	1.55520000
H	11.60240000	-3.56630000	2.90240000
C	13.28110000	-2.19700000	2.72300000
H	13.44460000	-1.16290000	2.39900000
H	13.61010000	-2.24010000	3.76660000
C	14.17310000	-3.11630000	1.88460000
H	13.71380000	-3.24060000	0.88610000
H	14.18410000	-4.11350000	2.33890000
C	-10.50600000	-0.82910000	4.29550000
H	-10.61780000	0.08600000	3.68070000
H	-10.64940000	-0.51150000	5.33510000
C	-11.60570000	-1.82060000	3.92240000
H	-11.46330000	-2.13990000	2.88190000
H	-11.49520000	-2.71750000	4.54070000

C	-13.00120000	-1.21580000	4.09150000
H	-13.05920000	-0.26480000	3.54930000
H	-13.18600000	-0.98450000	5.14590000
C	-14.13030000	-2.11030000	3.58520000
H	-13.91160000	-2.39410000	2.53970000
H	-14.15220000	-3.04210000	4.16180000
N	15.54500000	-2.60230000	1.83790000
H	16.15750000	-3.29290000	1.41480000
H	15.57160000	-1.78060000	1.23120000
N	-15.41770000	-1.42790000	3.75540000
H	-15.40320000	-0.56440000	3.21910000
H	-16.17920000	-1.99710000	3.39990000
N	15.34970000	0.03050000	-0.04730000
H	15.50450000	-0.05070000	-1.04810000
H	16.10340000	0.60230000	0.32120000
N	-14.51830000	0.37580000	1.06780000
H	-15.25390000	1.02920000	0.81740000
H	-14.91440000	-0.55540000	0.97370000

Photophysical properties of Py-1,4-DAB and Py-Spermine conjugates in PBS and DMSO:

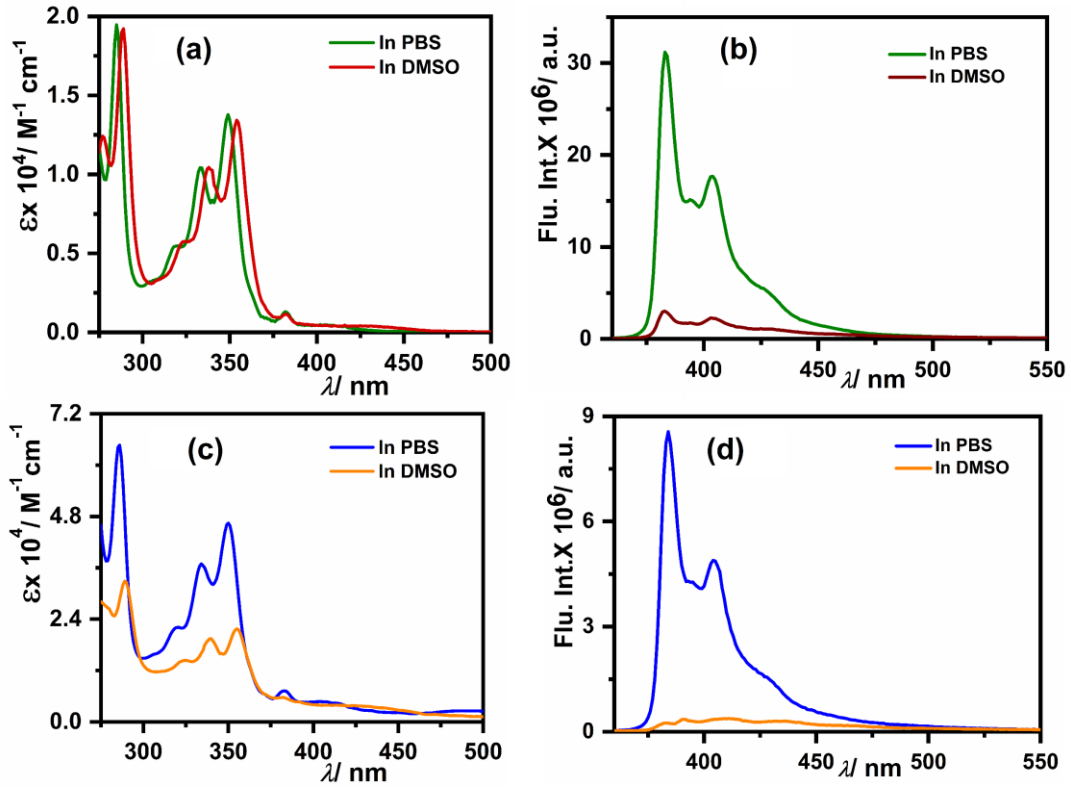

Fig. S61 (a) Absorption spectra of **Py-1,4-DAB** in PBS buffer and DMSO (b) emission spectra of **Py-1,4-DAB** in PBS buffer and DMSO (c) absorption spectra of **Py-Spermine** in PBS and DMSO (d) emission spectra of **Py-Spermine** in PBS and DMSO.

Table S10. Summary of photophysical data of **Py-BA**s in PBS and DMSO.

Conjugate/ solvent	λ_{max}^{abs}/ nm	λ_{max}^{em}/ nm	[a]Rel. QY (%)
Py-1,4-DAB/ PBS	349	383	17.2
Py-1,4-DAB/ DMSO	354	383	7.3
Py-Spermine/ PBS	349	384	11.9
Py-Spermine/ DMSO	354	410	9.9

Note: *[a]For the Rel. QY determination, Quinine sulphate in 0.5 M H_2SO_4 (QY = 0.54) was taken as the reference dye.[2] For the spectroscopic studies of the abovementioned conjugates,* ***Py-DA*** *(5 μM) and 1,4-DAB or spermine (10 μM) were added in $CHCl_3$. Then, the solutions were kept for 30 mins to obtain a full conversion from close* ***Py-DA*** *to open* ***Py-1,4-DAB*** *and* ***Py-Spermine*** *conjugates as was evident from fluorescence kinetics (**Fig. 5e**). Finally, the solvent was fully evaporated to dryness and conjugates were solubilized in PBS and DMSO separately which were further used for photophysical measurements.*

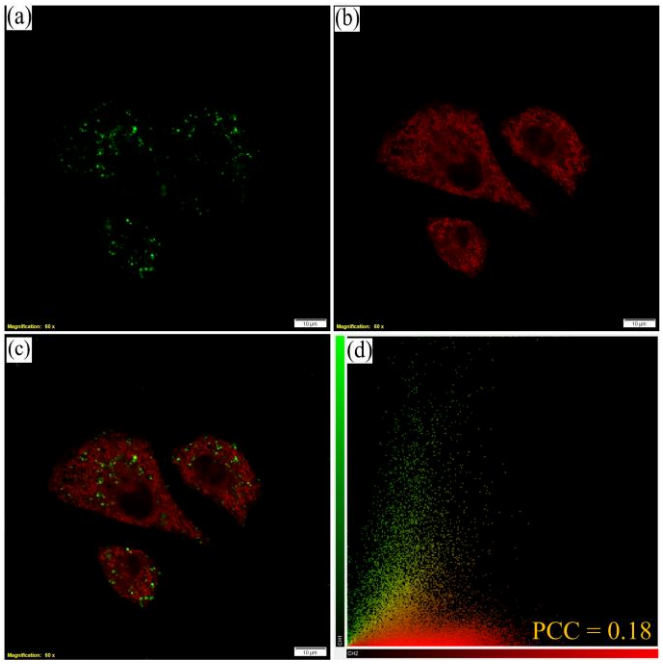

Fig. S62 CLSM images of live BHK-21 cells: (a) 5 μM **Py-Spermine** and (b) 0.3 μM MitoTracker Red, (c) merge image of (a) and (b), (d) scatter plot with Pearson's correlation coefficient 0.18 ± 0.03 (scale bar: 10 μm).

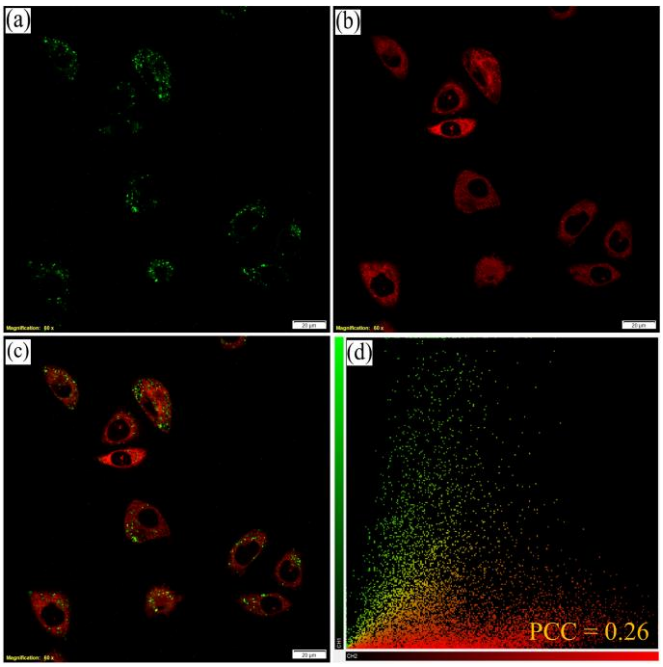

Fig. S63 CLSM images of live BHK-21 cells: (a) 5 μM **Py-Spermine** and (b) 0.3 μM ER Tracker Red, (c) merge image of (a) and (b), (d) scatter plot with Pearson's correlation coefficient 0.26 ± 0.04 (scale bar: 20 μm).

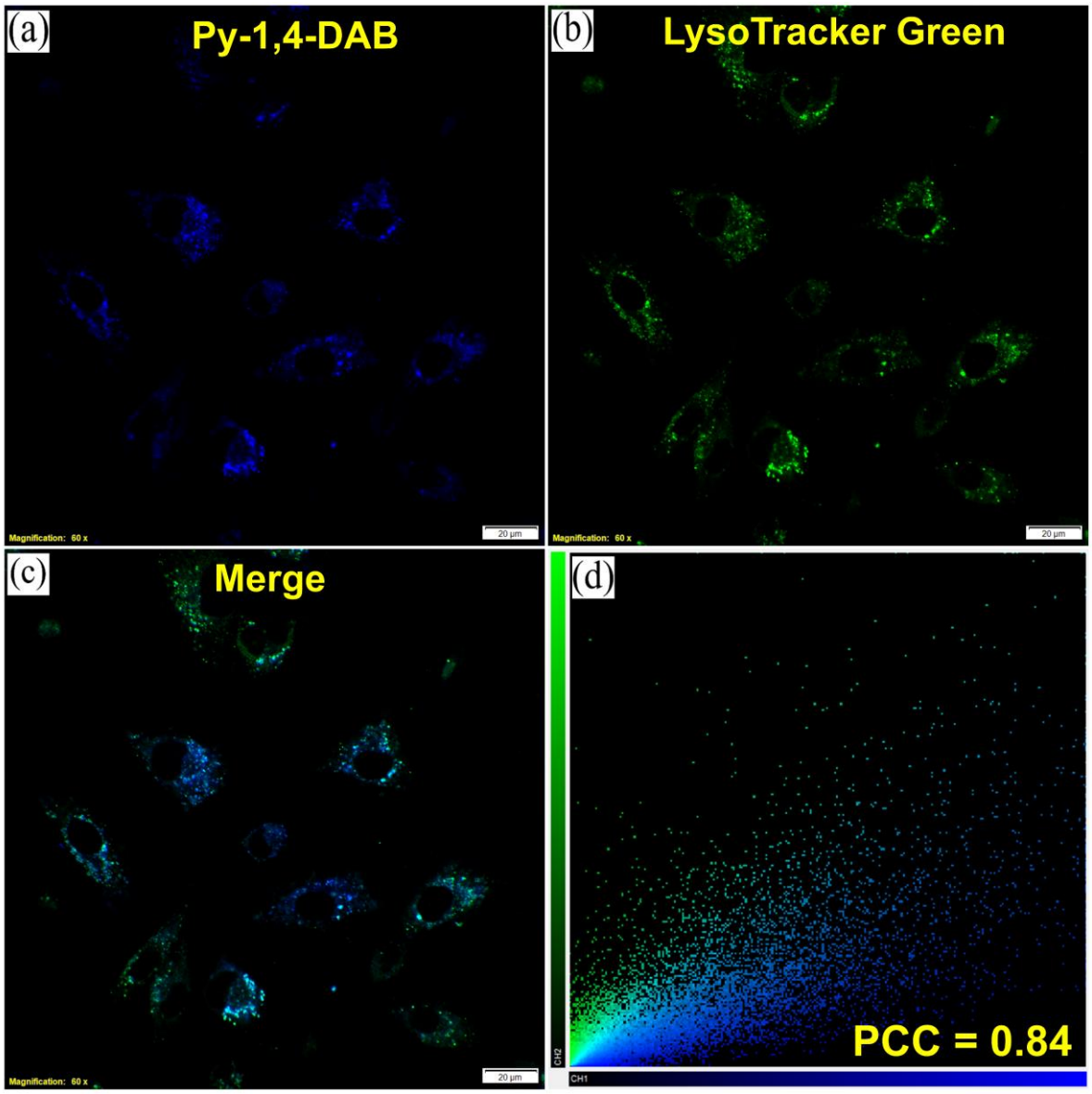

Fig. S64 CLSM images of live BHK-21 cells: (a) 5 μM **Py-1,4-DAB** and (b) 0.2 μM Lyso Tracker Green, (c) merge image of (a) and (b), (d) scatter plot with Pearson's correlation coefficient 0.84 ± 0.02 (scale bar: 20 μm).

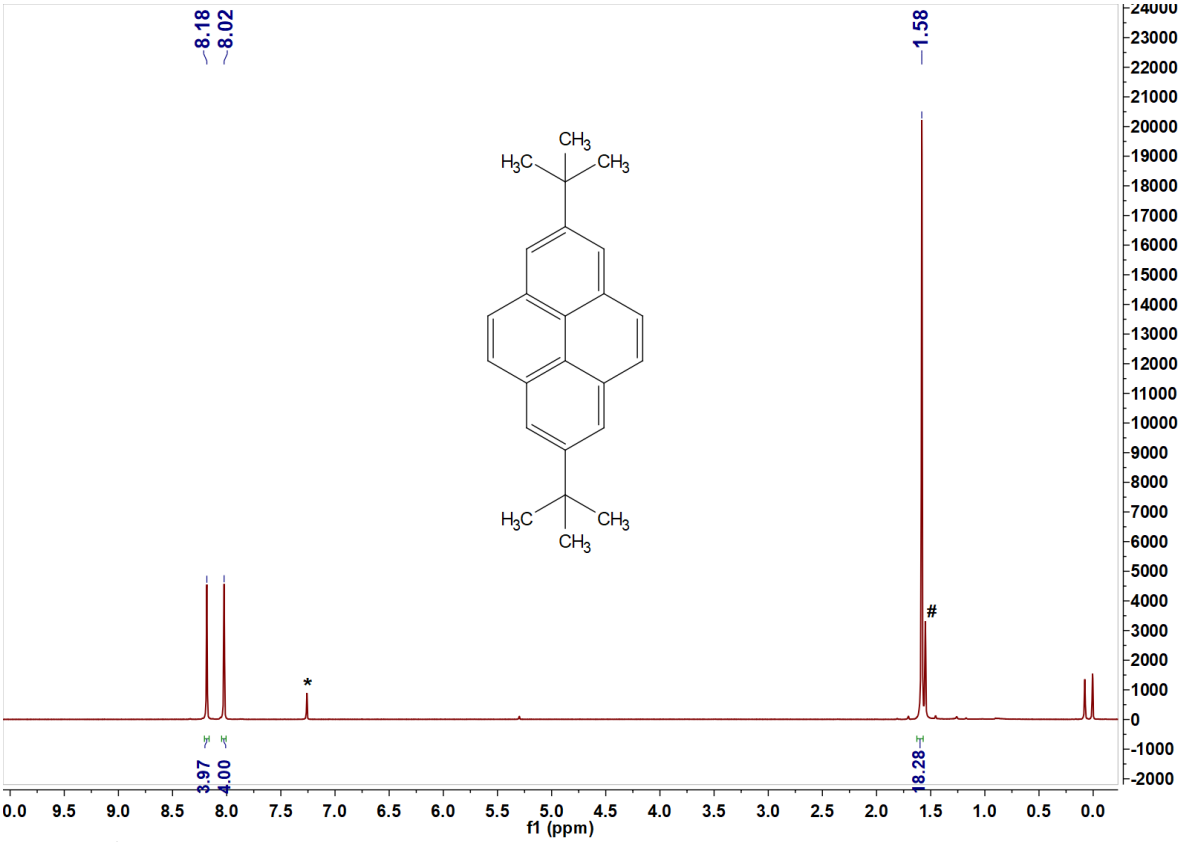

Fig. S65 ^{1}H NMR of 2,7-ditertbutylpyrene in $CDCl_3$ recorded at 500 MHz.

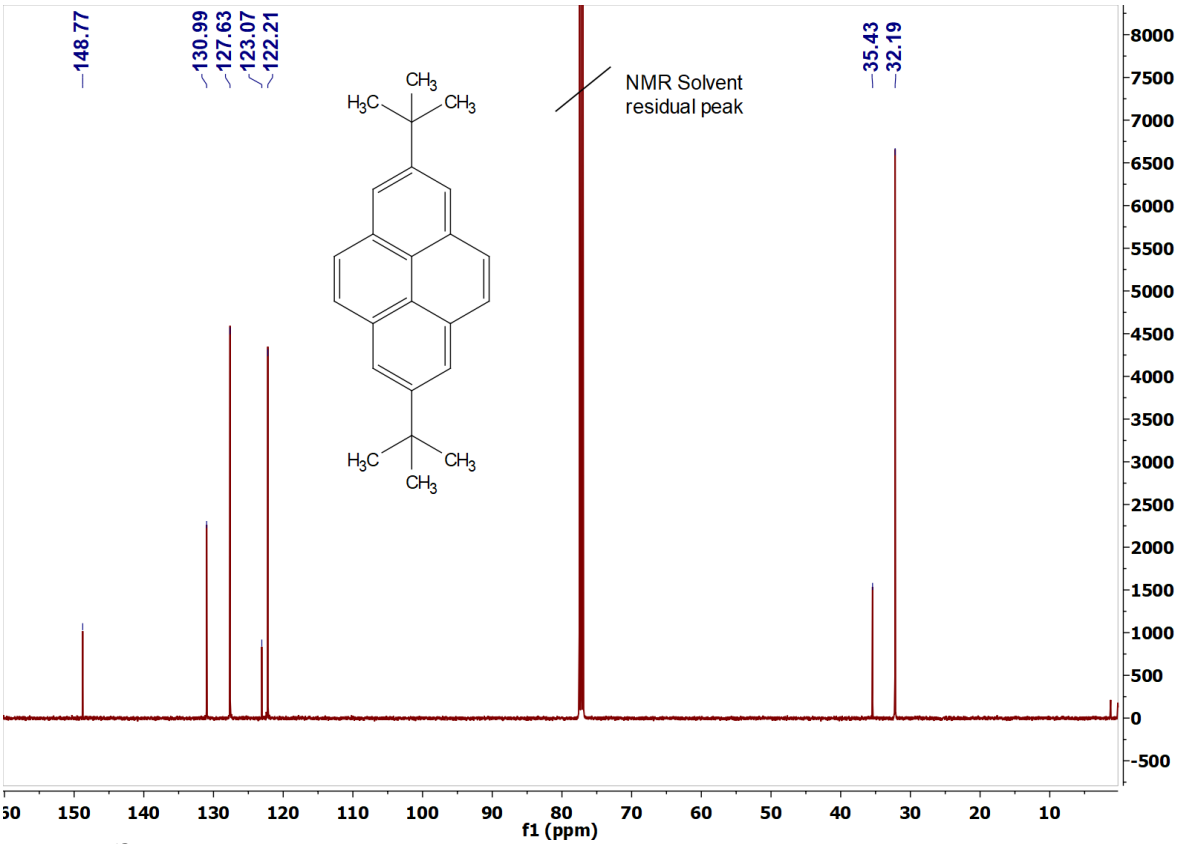

Fig. S66 ^{13}C NMR of 2,7-ditertbutylpyrene in $CDCl_3$ recorded at 126 MHz.

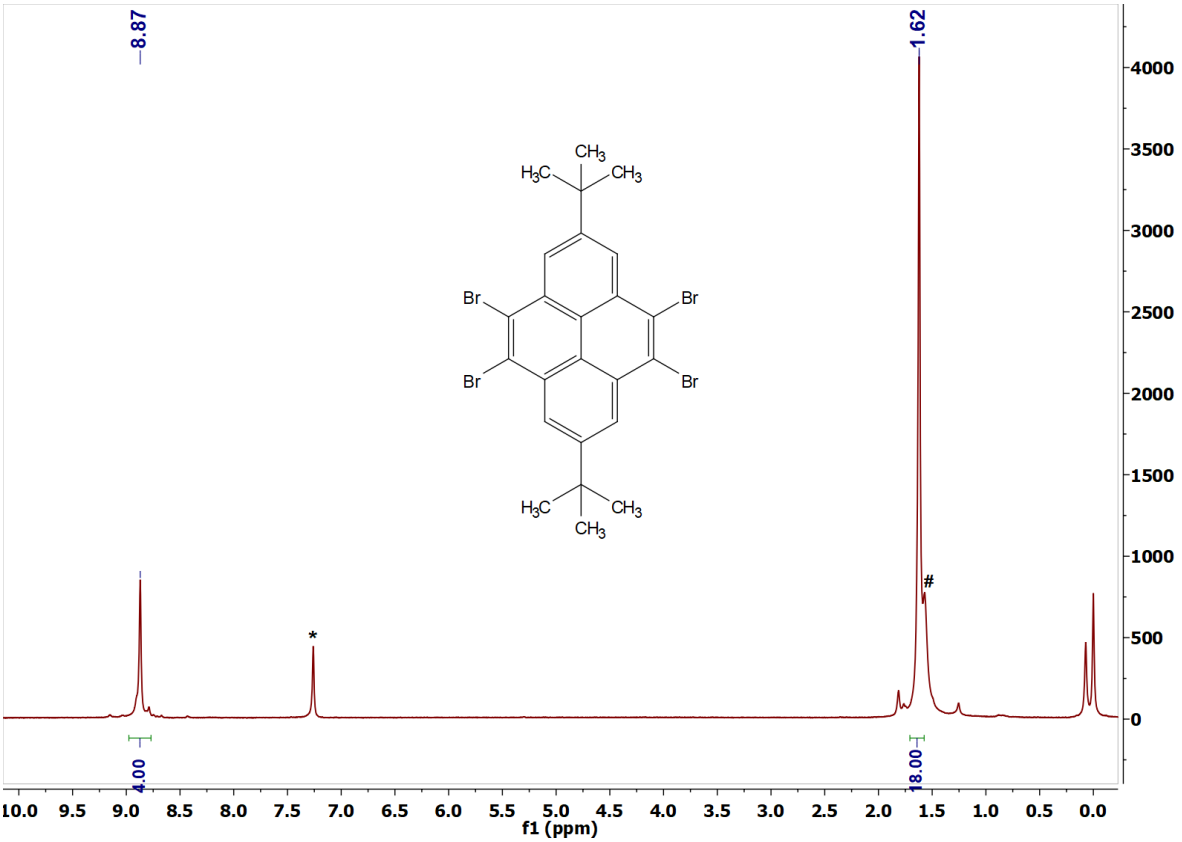

Fig. S67 ^{1}H NMR of 2,7-ditertbutyl-4,5,9,10-tetrabromopyrene in $CDCl_3$ recorded at 500 MHz.

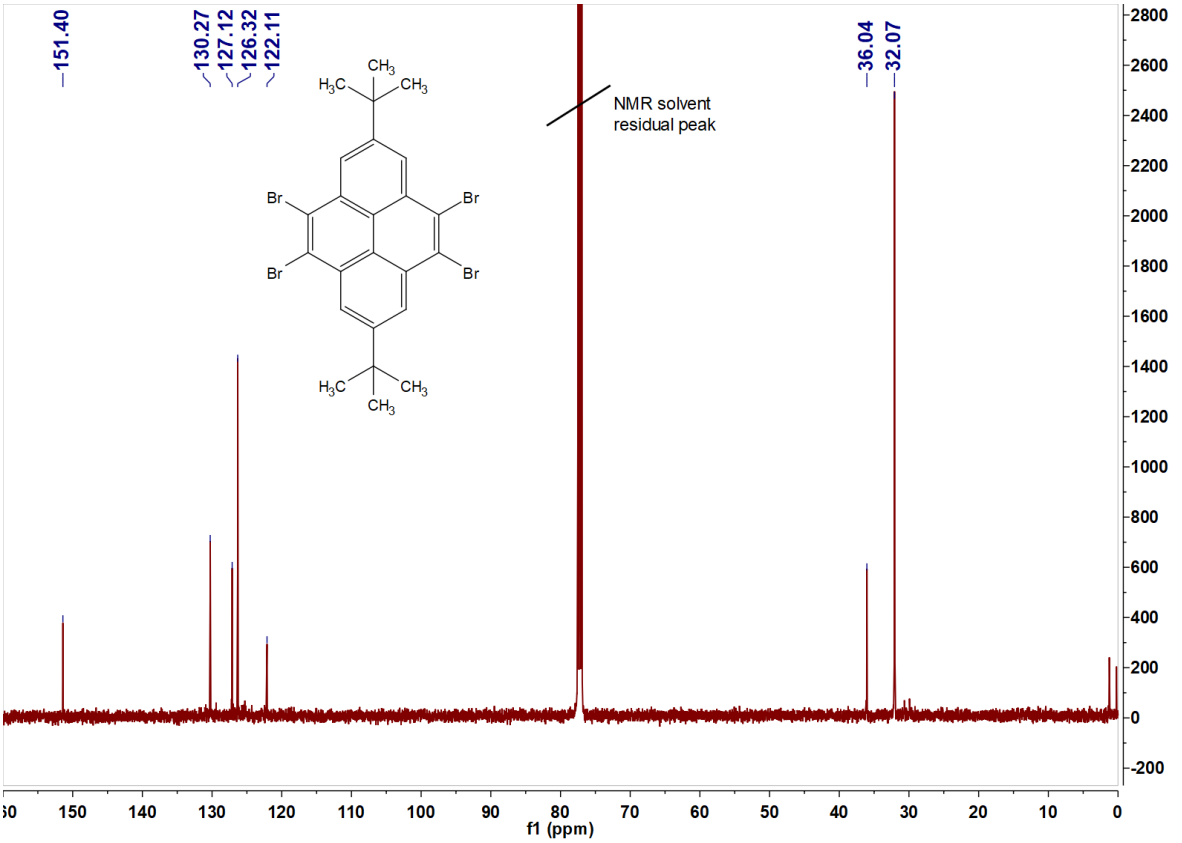

Fig. S68 ^{13}C NMR of 2,7-ditertbutyl-4,5,9,10-tetrabromopyrene in $CDCl_3$ recorded at 126 MHz.

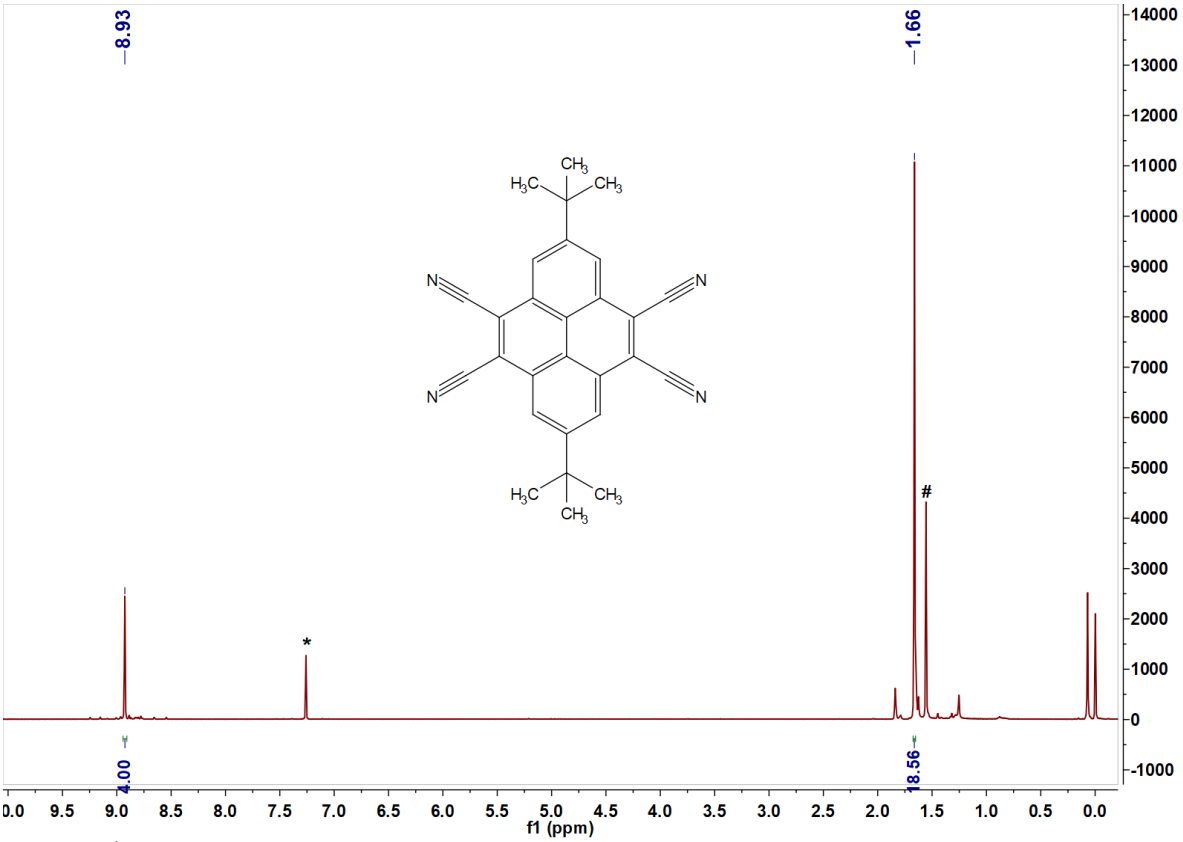

Fig. S69 ^{1}H NMR spectra of 2,7-ditertbutyl-4,5,9,10-tetracyanopyrene in $CDCl_3$ recorded at 500 MHz.

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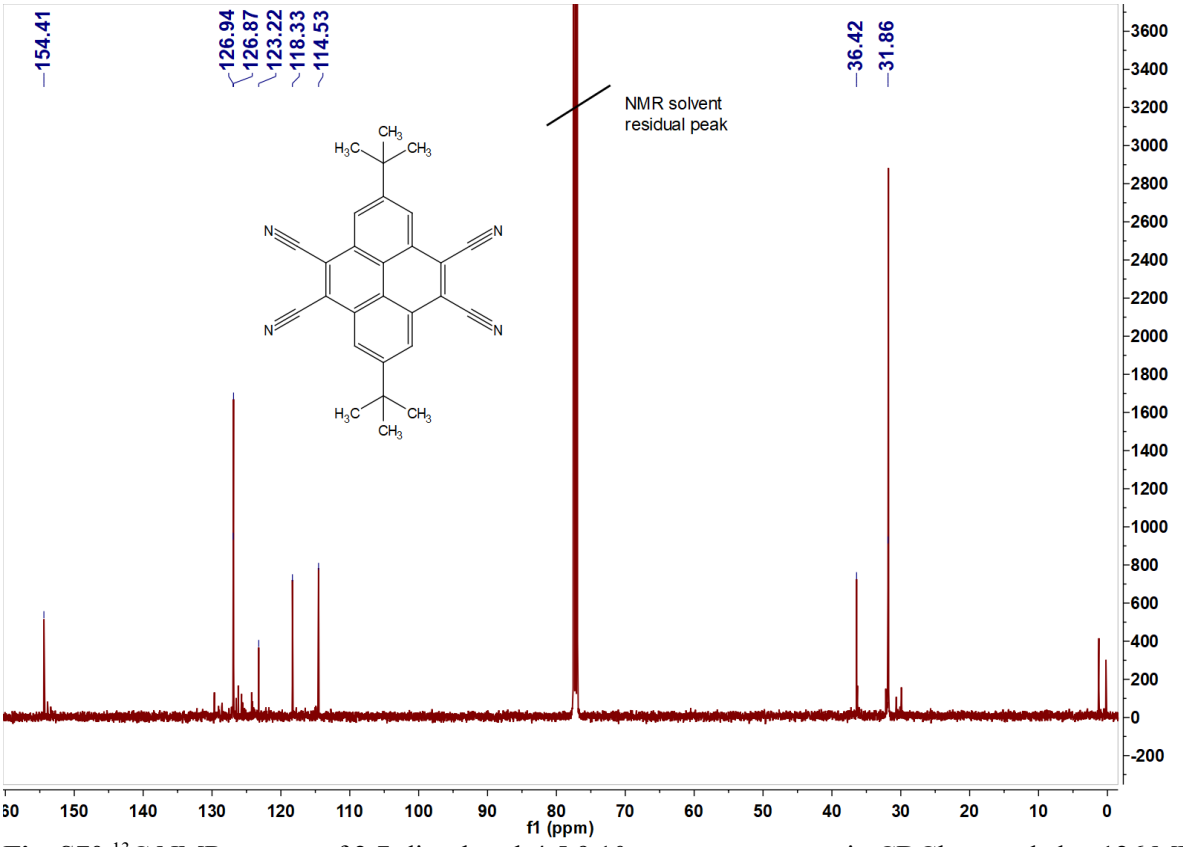

Fig. S70 ^{13}C NMR spectra of 2,7-ditertbutyl-4,5,9,10-tetracyanopyrene in $CDCl_3$ recorded at 126 MHz.

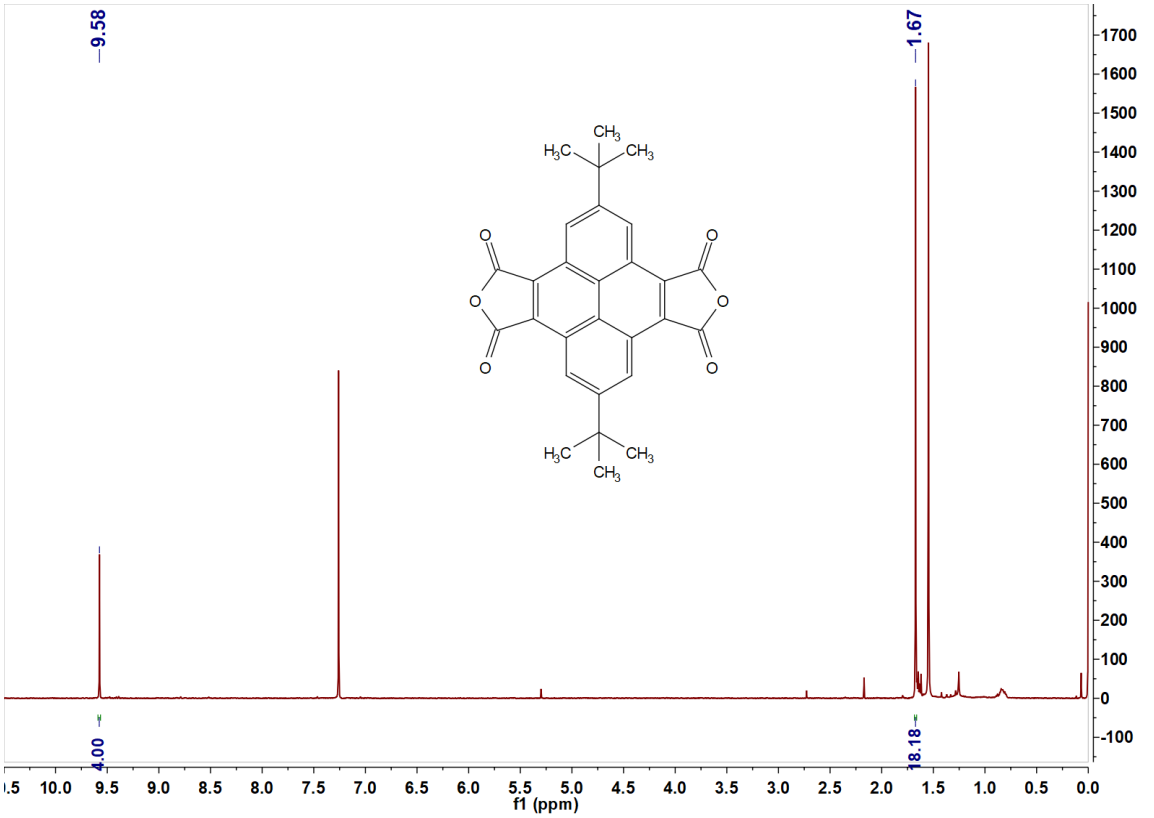

Fig. S71 ^{1}H NMR spectra of 2,7-ditertbutyl-4,5,9,10-pyrenetetracarboxylic dianhydride in $CDCl_3$ recorded at 500 MHz.

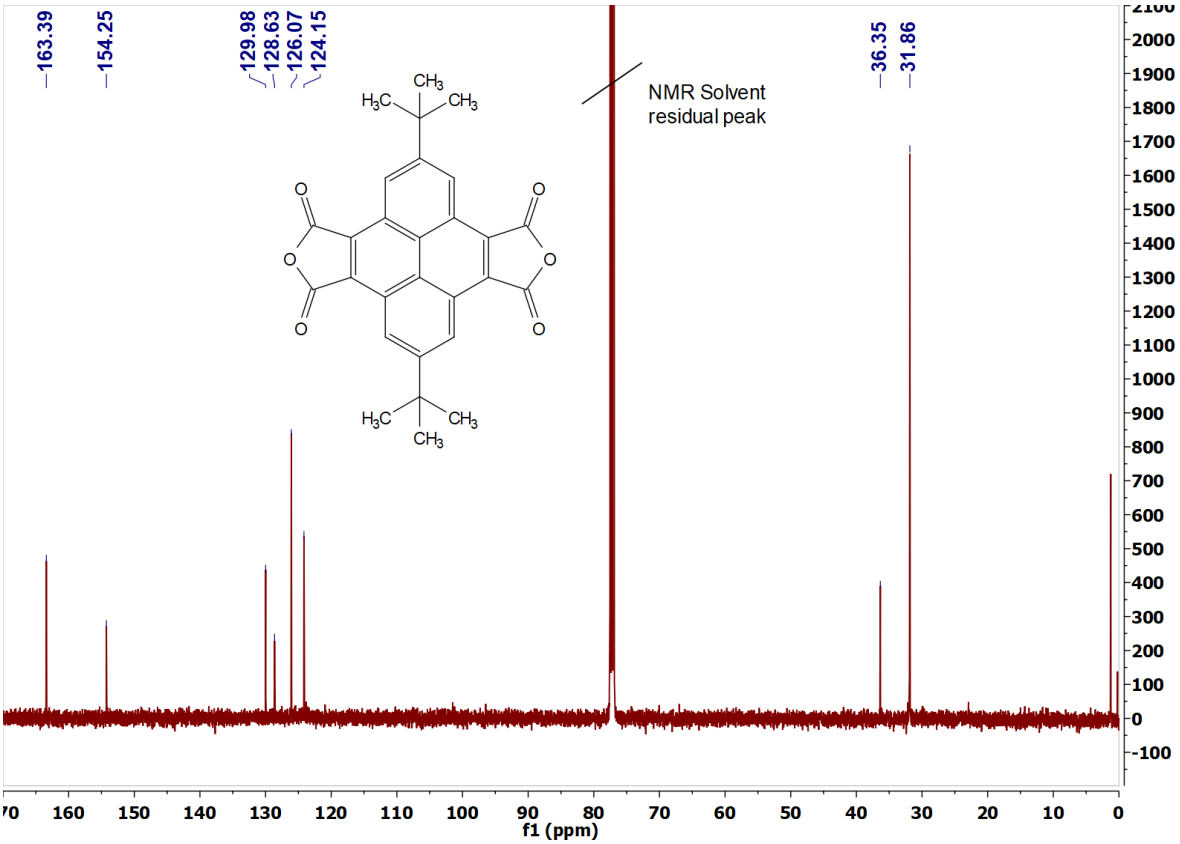

Fig. S72 ^{13}C NMR spectra of 2,7-ditertbutyl-4,5,9,10-pyrenetetracarboxylic dianhydride in $CDCl_3$ recorded at 126 MHz.

Note: * and # symbols represent the $CDCl_3$ and H_2O peaks in the ^{1}H NMR spectra.

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