Electronic Supporting Information

# Exploration of Dynamic Self-assembly Mediated Nanoparticle Formation Using Perylenemonoimide-Pyrene Conjugate: A Tool Towards Single-component White-light Emission

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## EXPERIMENTAL SECTION

**Materials:** Spectroscopic grade Methanol (MeOH), Acetonitrile (ACN), N,N-Dimethylformamide (DMF) and Toluene were purchased from Sigma-Aldrich. Spectroscopic grade Ethyl acetate (EtOAc), 1,4-dioxane, Chloroform ($CHCl_3$), Dimethyl sulfoxide (DMSO), Ethanol (EtOH) and Dichloromethane (DCM) were purchased from Sisco Research Laboratories Pvt. Ltd. The water used for experiments was obtained from Millipore water purification setup from Merck (resistivity 18 M$\Omega$ @ 25 ºC). THF was dried over metallic sodium using the standard protocol. Pyrene and perylene were acquired from Alfa Aesar and Sigma Aldrich respectively.

**Methods:** Stock solution of PMIAPy was made in dry THF in all the cases. A stock concentration of 0.5 mM was used and diluted as suited for all the spectroscopic measurements.

For SEM, the aged solution was taken as formed. For TEM and fluorescence microscopy, we used 4X and 2X dilution respectively of the self-assembly containing solution. All of these solutions were obtained from aging of the 10 $\mu$M PMIAPy solution in dry and distilled THF at room temperature (25 °C). For concentration dependent SEM, self-assembly containing solutions were obtained from aging of the 5 $\mu$M, 10 $\mu$M, 20 $\mu$M PMIAPy solution in dry and distilled THF at room temperature (25 °C).

**Steady-state and kinetic absorption and fluorescent measurements:** Steady-state absorption measurements were executed using Cary 5000, and kinetic absorption measurements were carried away in Cary 60 spectrophotometer from Agilent Technologies using quartz cuvette of 1 cm path length. Dilute solution of samples was used to avoid any inner-filter effect or to avoid aggregation effect. Steady-state and kinetic fluorescence measurements were performed using HORIBA Jobin Yvon Fluorolog and Horiba Fluoromax using 1 cm path length quartz cuvette. The excitation, emission slit width and integration time were varied accordingly. All the experiments were carried out at room temperature unless otherwise mentioned.

**Time-resolved fluorescence measurement:** Time-resolved fluorescence measurements were done using the time-correlated single photon counting (TCSPC) setup from Horiba Jobin Yvon. The instrument response function (IRF) was measured before the start of measurements with a particular laser, using a dilute suspension of Ludox (from Sigma). The 373 nm and 509 nm pico-second pulsed lasers were used as the excitation source with a setup target of 10,000 counts. The emission polarizer was set at the magic angle (54.7 °) with respect to excitation polarizer. The decay profile was fitted by using iterative deconvolution method in supplied software DAS v6.2 utilizing the following exponential function.

$$I_t/I_0 = \Sigma a_i \exp(-t/\tau)$$

Where $I_t$ and $I_0$ are the fluorescence intensity at time t and 0, t is time, $a_i$ and $\tau$ are the contributing amplitude and lifetime. The fitted data with the chi-square value ($\chi^2$) ranging from 0.9-1.2 is considered. TCSPC experiments were performed at room temperature (298 K).

**Hydrodynamic Size of NPs:** Dynamic light scattering was performed using a Delsa™ Nano (from Beckman Coulter). A stock solution of 15 $\mu$M PMIAPy is incubated in dry and distilled THF for *ca.* 22 h and after seeing the colour change of the solution the solution was concentrated to good count rate from the scattering. Typical count rates were adjusted around 100-300 kHz. Each autocorrelation function was acquired for 10 s, and averaged over 10 measurements. The resulting autocorrelation function was fitted using OmniSize 3.0 software (supplied with Beckman Coulter). Solvodynamic diameter was obtained in THF from a number-weighted size distribution analysis.

**Microscopy:** For SEM the samples were drop casted on cover-slips placed upon carbon tape, dried overnight under vacuum and coated with gold by sputter coating. Samples were visualized under a scanning electron microscope (SEM) from Carl Zeiss at a suitable working voltage of 20 kV. For TEM, samples were drop cast on carbon-coated copper grids and examined with FEI Talos F200X TEM setup. Samples for fluorescence microscopy were drop cast on a glass slide, dried and covered with glass cover-slips. For fluorescence microscopy, samples were inspected with Olympus Fluoview FV3000 fluorescence microscope setup in the blue channel (DAPI 405), red channel (Alexa-561) and bright field in the automatic mode.

**CIE chromaticity Index calculation:**[1] The CIE chromaticity index values were calculated using following formulas

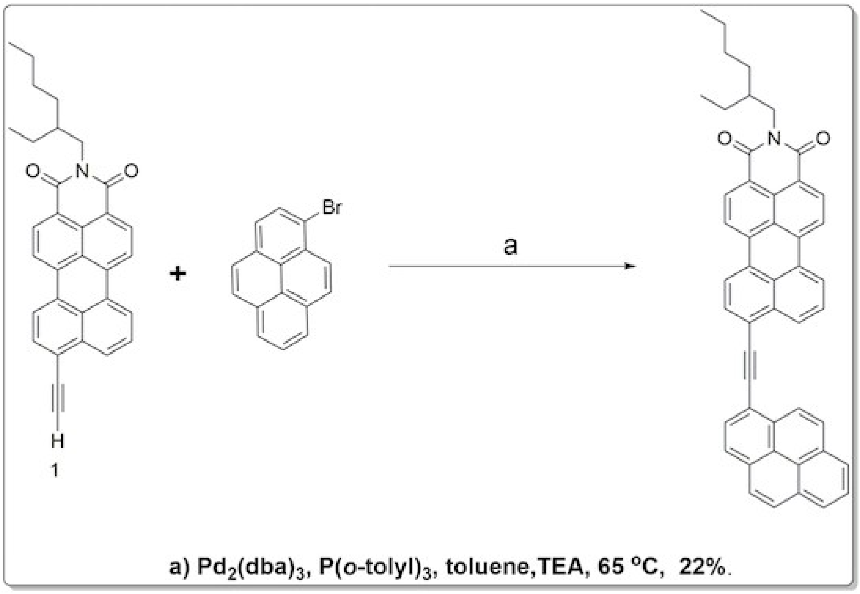
$$X = \Sigma_{k=1}\phi_k(\lambda)B_k(\lambda)$$
$$Y = \Sigma_{k=1}\phi_k(\lambda)G_k(\lambda)$$
$$Z = \Sigma_{k=1}\phi_k(\lambda)R_k(\lambda)$$

Where X, Y, Z are tristimulus values, $\phi_k(\lambda)$ spectra distribution of color stimulus which we got from the fluorescence spectra of species of interest and $B_K(\lambda)$, $G_K(\lambda)$, and $R_K(\lambda)$ are color-matching functions of a standard colorimetric observer. Coordinates of the color stimulus are (x, y, z) where x= (X/X+Y+Z), y= (Y/X+Y+Z), and z= (Z/X+Y+Z)

**Structural optimization:** The optimized ground state structure for PMIAPy was accomplished using GaussView 5.0.8 software. Density functional theory (DFT)/ B3LYP method was used for optimizing the structure with 6-311G basis set. Frontier orbital energy value was matched with experimental value.

**Synthesis of PMIAPy:**

**Scheme. S1:** Synthesis of PMIAPy



a) $Pd_2(dba)_3$, P(*o*-tolyl)$_3$, toluene,TEA, 65 °C, 22%.

**Procedure:** Compound 1[2] (60 mg, 0.1312 mmol), 1- bromopyrene (35.14 mg, 0.1249 mmol) were taken in a dry Schlenk tube. Dry toluene (5 ml), triethylamine (1 ml) was added in the reaction mixture. The resulting solution was degassed by freeze pump thaw cycles for three times. Then under $N_2$ atmosphere $Pd_2(dba)_3$ (11.44 mg, 0.0125 mmol), P(*o*-tol)$_3$ (29.58 mg, 0.0811 mmol) were added in the Schlenk tube. Then reaction mixture was evacuated and flushed with $N_2$ three times. After that reaction mixture was heated at 65 °C for 18 h and upon completion of the reaction the solvent was evaporated in rotary evaporator and then purified by column chromatography (Silica, $CHCl_3$ used as eluent) afforded the desired compound (34 mg, 22 %)

$^1$H NMR (500 MHz, $CDCl_3$): δ 8.66 (dd, $J$ = 17.2, 8.7 Hz, 2H), 8.50 (dd, $J$ = 15.1, 7.6 Hz, 3H), 8.40 – 8.31 (m, 3H), 8.26 (d, $J$ = 7.9 Hz, 1H), 8.20 (dd, $J$ = 14.4, 7.9 Hz, 3H), 8.11 (dd, $J$ = 16.0, 8.4 Hz, 2H), 8.02 (dt, $J$ = 17.9, 7.8 Hz, 3H), 7.81 (t, $J$ = 7.8 Hz, 1H), 4.14 (ddd, $J$ = 20.3, 12.9, 7.0 Hz, 2H), 1.98 (m, 1H), 1.44 – 1.39 (m, 4H), 1.35 – 1.30 (m, 4H), 0.96 (t, $J$ = 7.5 Hz, 3H), 0.92 – 0.88 (t, 3H).

Chemical formula-$C_{48}H_{35}NO_2$ Calculated mass-657.2668 and Obtained mass- m/z 658.2762$[M+H]^+$

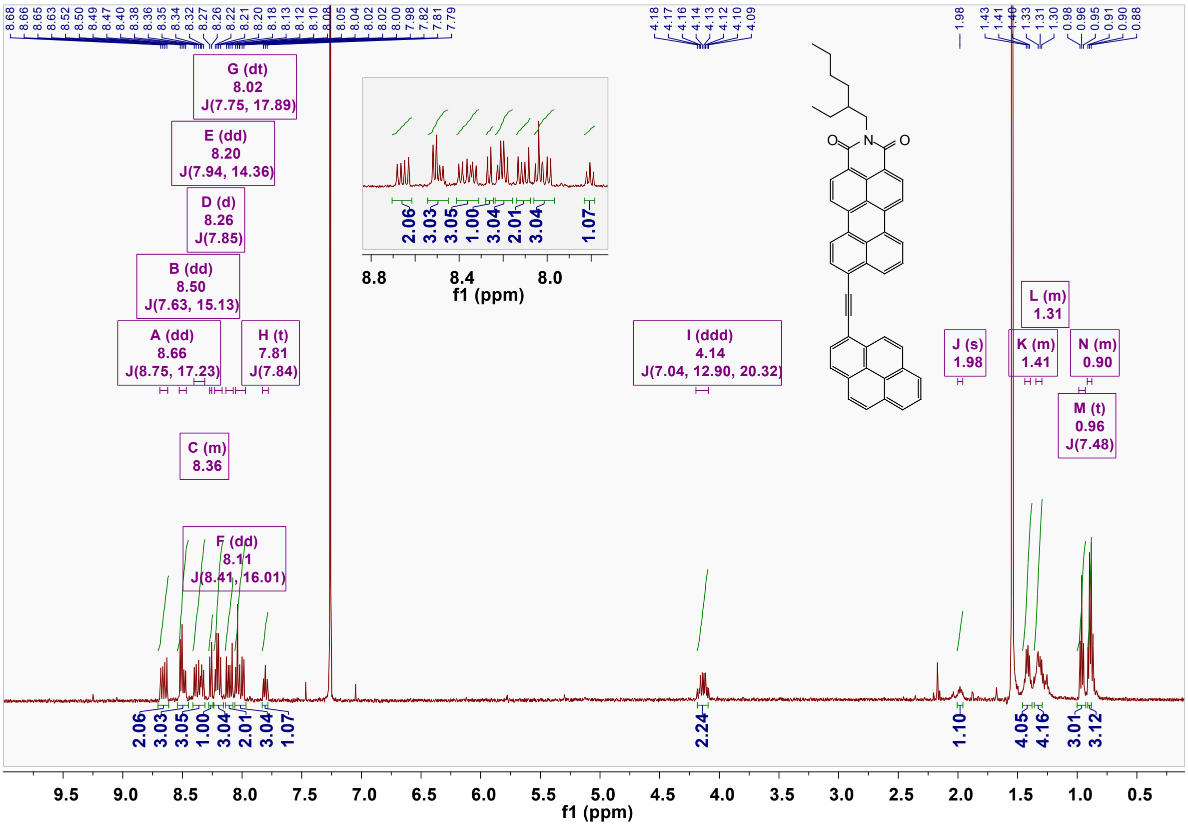


**Fig. S1** $^1$H NMR spectrum of PMIAPy

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | APCI | Ion Polarity | Positive | Set Nebulizer | 2.5 Bar |
| Focus | Not active | Set Capillary | 4000 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set Collision Cell RF | 600.0 Vpp | Set Divert Valve | Waste |

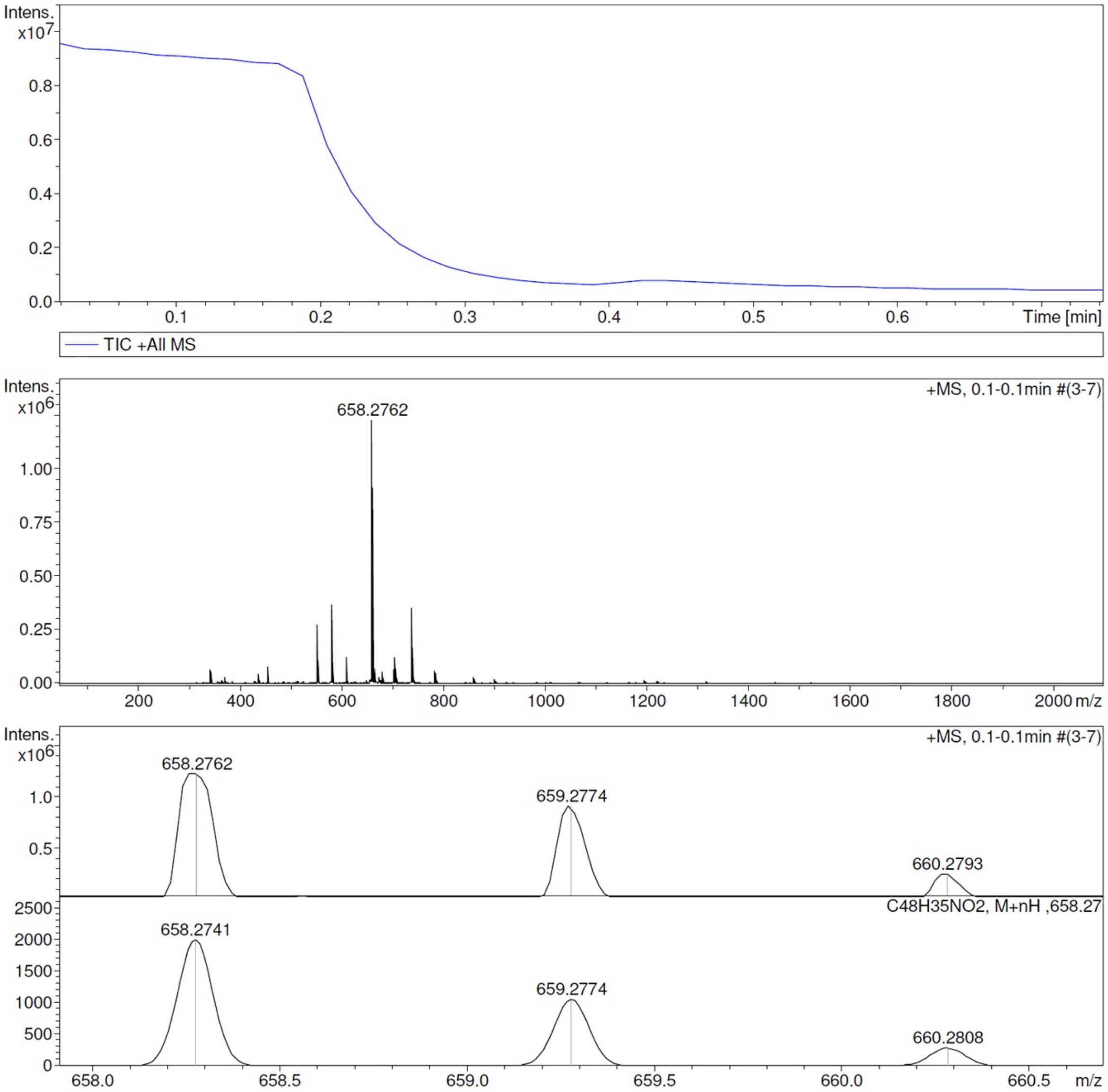


**Fig. S2** Mass spectrum (APCI) of PMIAPy

**Optical properties of PMIAPy:**

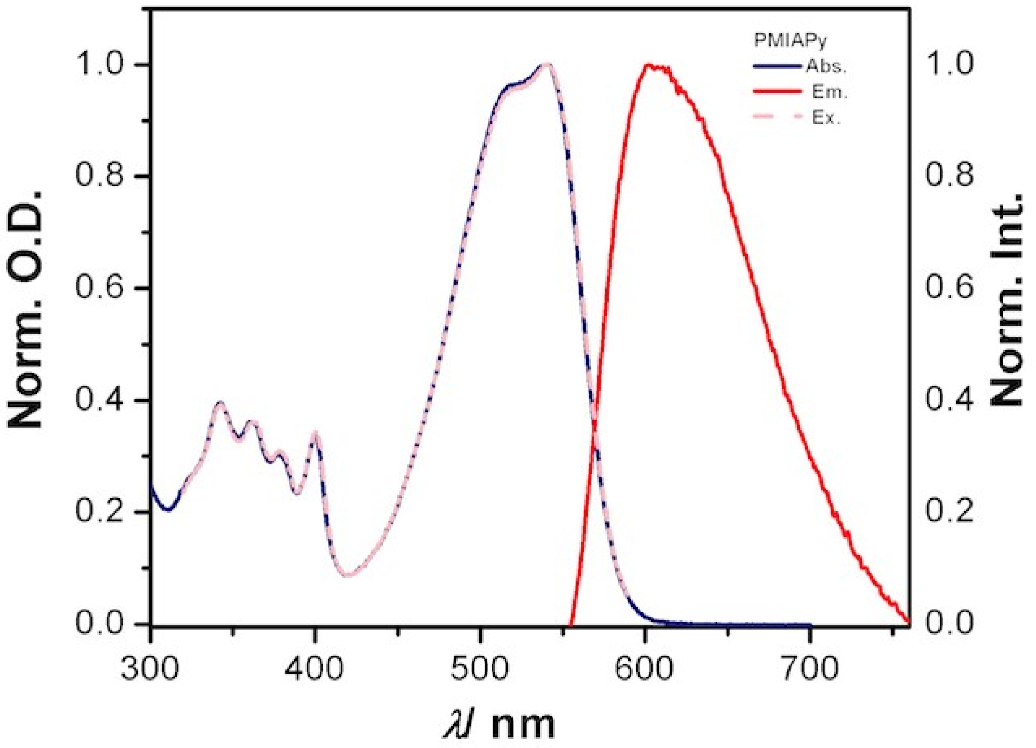


**Fig. S3** Optical properties of PMIAPy**.** Merged representation of absorption spectra ($\lambda_{max}$ = 540 nm), emission spectra ($\lambda_{em}$ = 605 nm) and excitation spectra (monitored at 605 nm) of PMIAPy in dry THF.

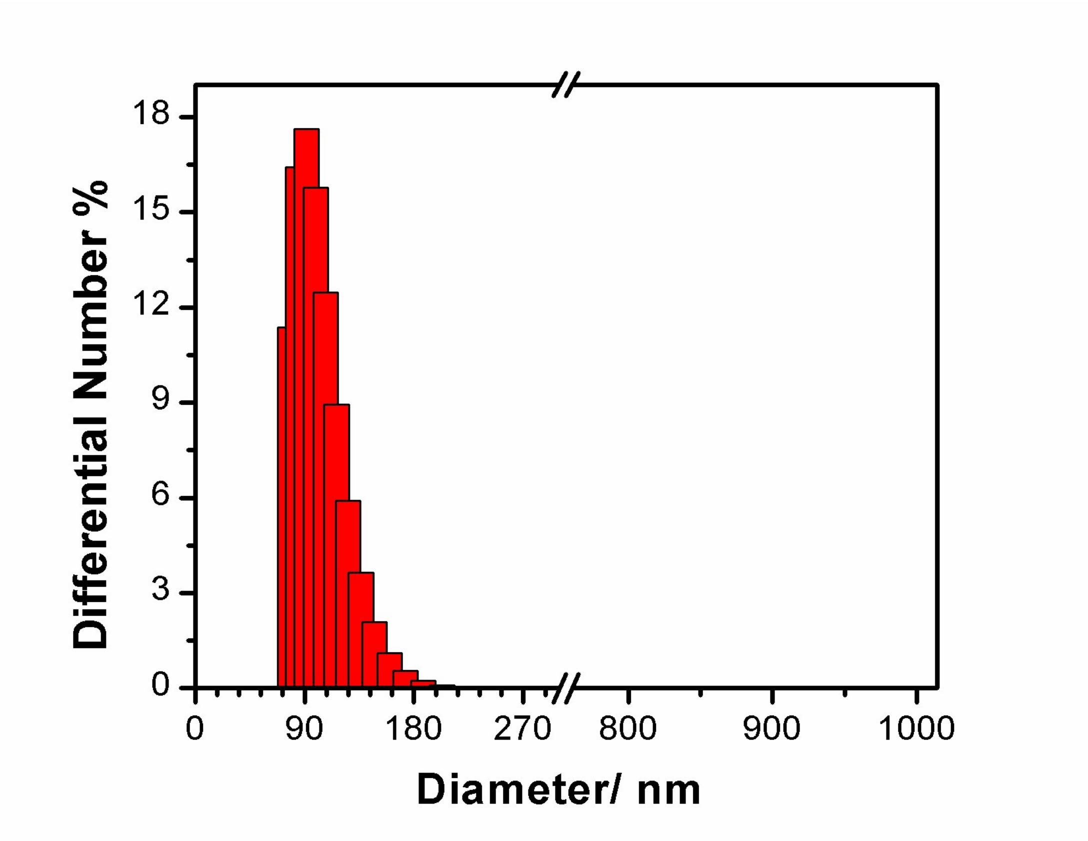


**Fig. S4** Solvodyanmic size of self-assembled PMIAPy NPs (diameter 100±25 nm) obtained using DLS measurement in THF a RT after ~22 h of incubation.

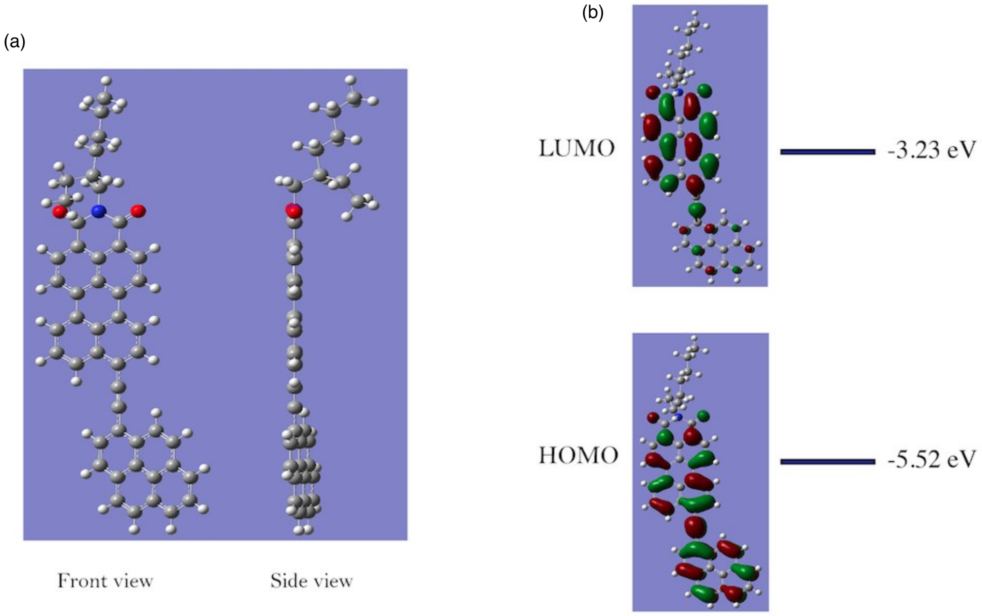


**Fig. S5** (a) Optimized structure ground-state structure of PMIAPy (front view and side view) achieved with DFT/B3LYP method with 6-311G basis set using GaussView 5.0.8, a non-linerarity is clearly evident and (b) frontier molecular orbital of PMIAPy, (above) LUMO with -3.23 eV energy and (below) HOMO with -5.52 eV energy.

**Lifetime decay profile:**

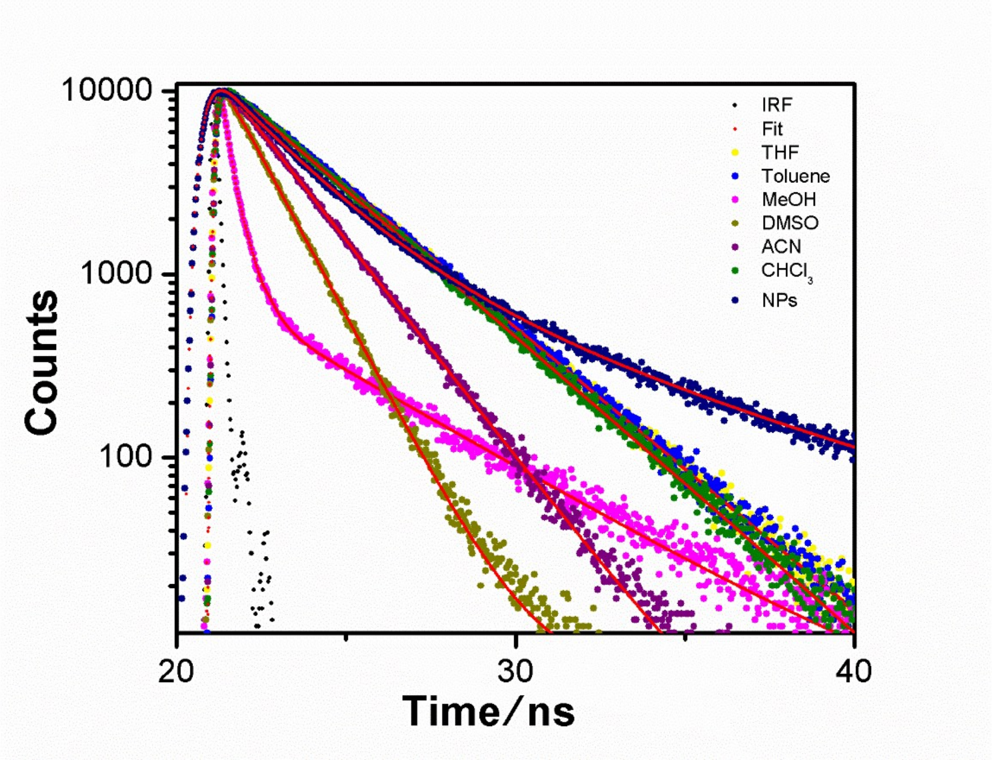


**Fig. S6** Fluorescence decay profile of PMIAPy in different solvents and NPs in THF

**Table. T1**: Representative table for lifetime decay of PMIAPy in different solvents and NP in THF.

| Species in Solvent | $\tau_{avg}$ (ns) | $\chi^2$ Value | Exponential | $\lambda_{mon}$ (nm) |
|---|---|---|---|---|
| PMIAPy in THF | **2.8** | **1.07** | **Mono** | **605** |
| PMIAPy in MeOH | **3.6**[a] | **1.13** | **Tri** | **695** |
| PMIAPy in Toluene | **2.8** | **1.06** | **Mono** | **580** |
| PMIAPy in $CHCl_3$ | **2.7** | **1.07** | **Mono** | **615** |
| PMIAPy in DMSO | **1.2** | **1.15** | **Mono** | **670** |
| PMIAPy in ACN | **1.8** | **1.08** | **Mono** | **660** |
| NPs in THF | **4.9**[b] | **1.14** | **Bi** | **470** |

[a] For PMIAPy in MeOH, three species with 0.42 ns (36.5 %), 4.1 ns (35.9 %), and 0.19 ns (27.6 %) lifetime contributed for the average lifetime of 3.6 ns. [b] For NP the average lifetime is contributed by two species with 2.1 ns (68.3 %), and 6.7 ns (31.7%) lifetime.

## Effect of concentration in aggregation:

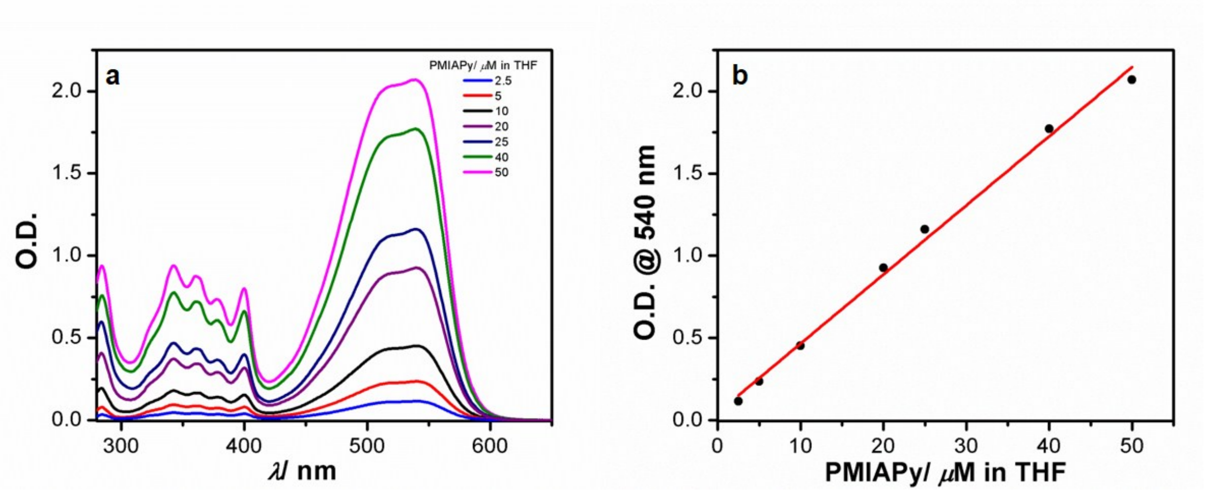


**Fig. S7** Effect of concentration in aggregation of PMIAPy in THF. (a) PMIAPy concentration-dependent UV-Vis spectra; (b) A linear plot of dye concentration and O.D. at 540 nm to validate the linearity any deviation from Beer-Lambert law

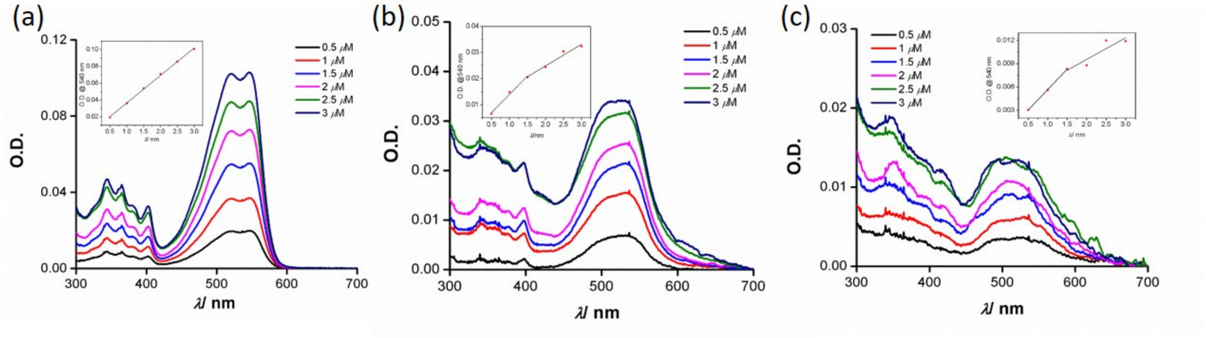


**Fig. S8.** Effect of concentration in aggregation and deviation from Beer Lambert's law. PMIAPy concentration dependent UV-Vis. spectra and a plot between PMIAPy concentration and O.D. at 540 nm to validate the deviation of Beer-Lambert's law due to aggregation in inset for (a) Toluene, (b) ACN, and (c) MeOH.

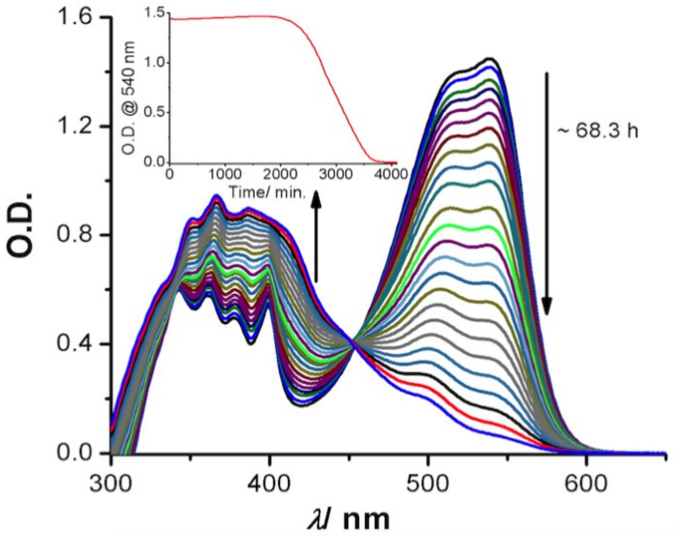


**Fig. S9** Evolution of UV-Vis. spectra of 30 μM PMIAP during NP formation at 25 °C in dry THF. Inset shows the spectral kinetics at 25 °C in dry THF.

## Kinetic study:

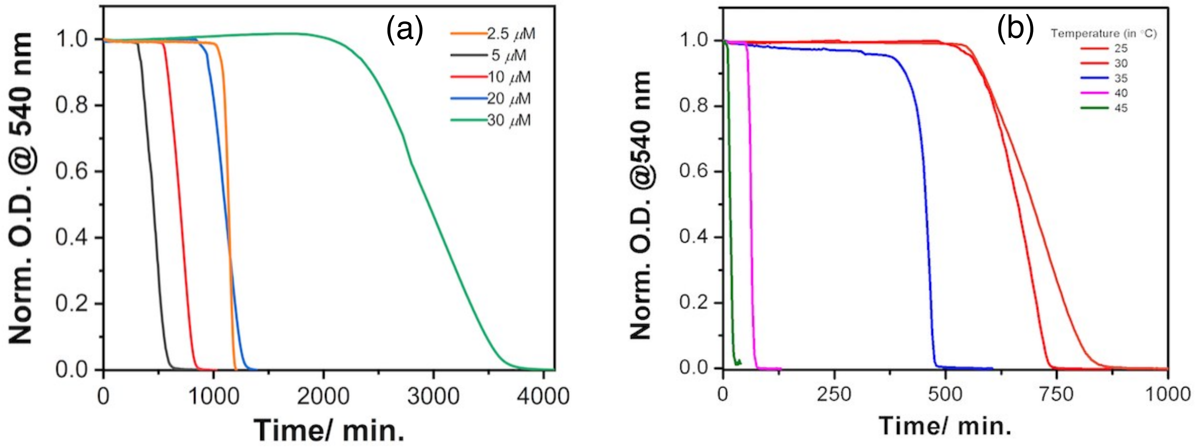


**Fig. S10** Kinetic monitoring *via* changes in O.D. @ 540 nm. (a) kinetic study with different concentration (5μM, 10 μM, 20 μM, 30 μM) PMIAPy in dry THF (b) kinetic study at different temperature (25 °C, 30 °C, 35 °C, 40 °C, 45 °C)

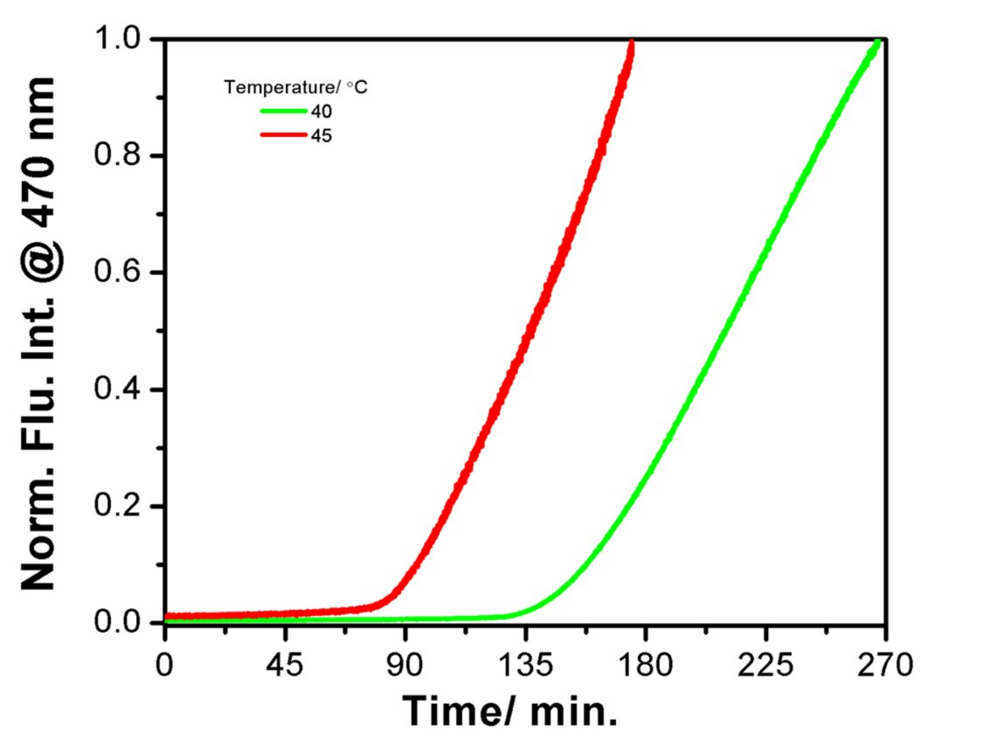


**Fig. S11** Kinetic monitoring *via* changes in fluorescence intensity @ 470 nm. Kinetic study at different temperature of 40 °C and 45 °C

## Concentration-dependent scanning electron micrograph (SEM):

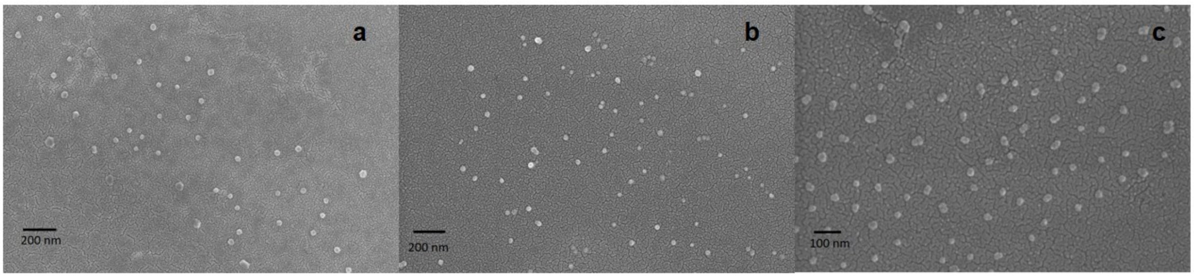


**Fig. S12** SEM images of NPs at different PMIAPy concentration. Self-assembled from (a) 5 $\mu$M, (b) 10 $\mu$M and (c) 20 $\mu$M PMIAPy concentration in dry THF.

## Transmission electron micrograph (TEM):

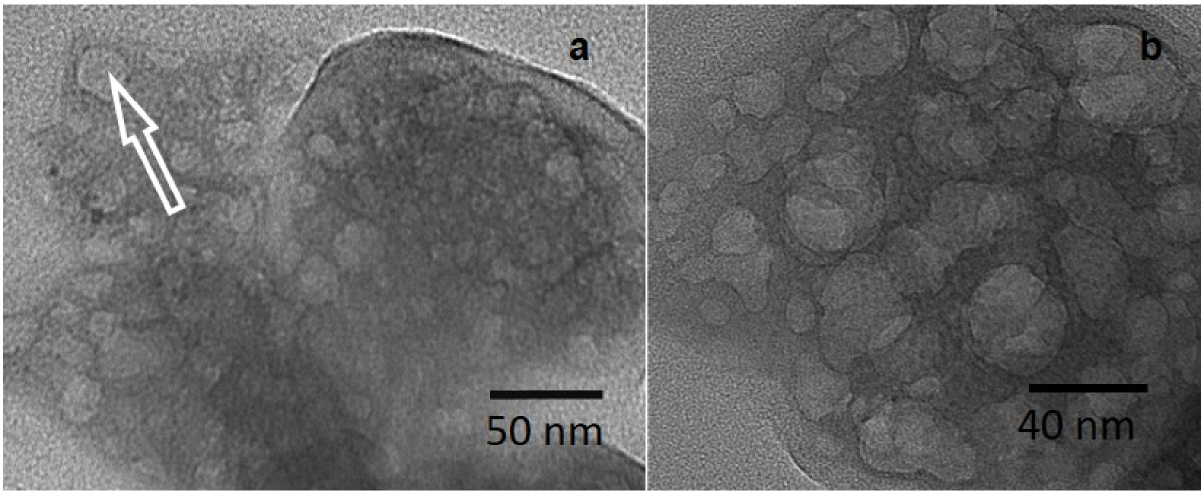


**Fig. S13** TEM of NPs generated from 10 $\mu$M PMIAPy in dry THF. Images of (a) unyoking of NPs and (b) NPs with the size distribution of 30±10 nm. The NP solution in THF was drop cast to visualize.

## Robustness:

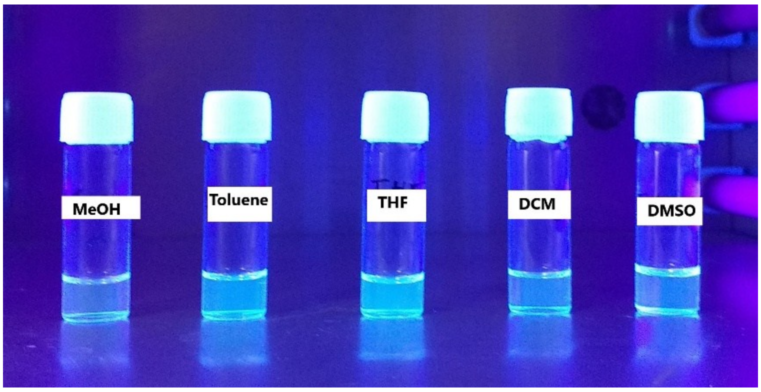
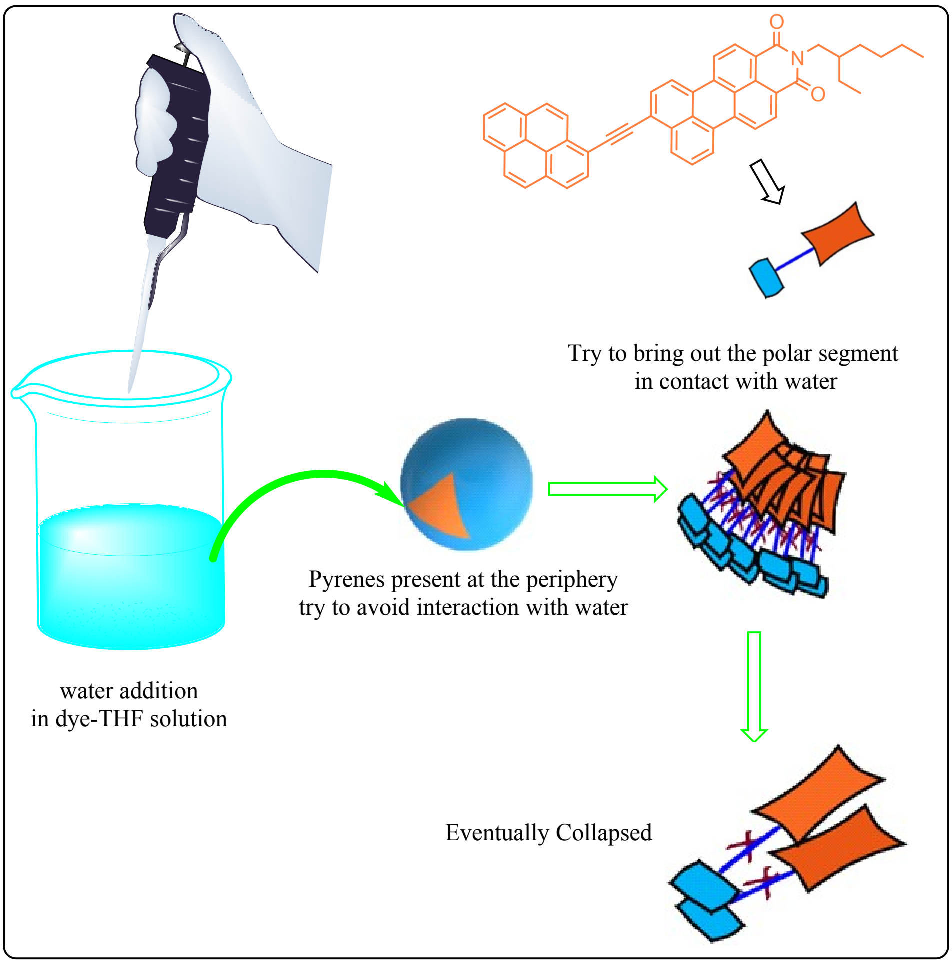


**Fig. S14** Photograph of UV-illuminated NPs dissolved in different solvents.

## Reversible dis-assembly of nanoparticles:



**Scheme S2** Interaction of nanoparticles with hydrophilic local environment generated due to excess addition of water in dry THF

## References:

1. CIE (1931). *Commission internationale de l'Eclairage proceedings, 1931*. Cambridge: Cambridge University Press.
2. K. Pal, V. Sharma and A. L. Koner, *Chem. Commun.*, 2017, **53**, 7909-7912.