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Ultrafast Symmetry-Breaking Charge Separation in PMI-embedded Multichromophores: Impact of Regioisomerism

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I. Materials and methods

The chemical reagents perylenetetracarboxylic dianhydride, 1,2-diiodobenzene, 1,3-diiodobenzene, 1,4-diiodobenzene, triisopropylsilyl-acetylene (TIPS-ac) and tetrabutylammonium fluoride (TBAF) in THF were purchased from Sigma-Aldrich and used as received. $Ru(CO)(H)_2(PPh_3)_3$, 4-methyl-1-pentene were bought from TCI chemicals and tris(dibenzylacetone)dipalladium (0) [$Pd_2(dba)_3$], Tri(*o*-tolyl)phosphine [P(*o*-tolyl)$_3$] and 1,3,5-tribromobenzene were purchased from Alfa-Aesar and used as received. Bromine and triethylamine (TEA) were purchased from Spectrochem. Ethyl acetate, hexane, chloroform, methanol solvents for column chromatography were purchased from Finar Chemicals. The spectroscopic grade solvents such as toluene (Tol), chloroform ($CHCl_3$) and dimethylformamide (DMF) were bought from Sisco Research Laboratories (SRL) and used for spectroscopic measurements after received. The NMR solvent $CDCl_3$ was purchased from Sigma Aldrich. Unless otherwise mentioned, the *ortho*-functionalization reaction was performed in 5 mL microwave vials and the Sonogashira-Hagihara cross coupling reaction was carried out in Schlenk tube under inert atmosphere. The anhydrous solvents used here such as mesitylene, toluene, and dichloromethane (DCM) were dried by keeping them with CaH_2 for overnight stirring followed by distillation. TEA was dried by overnight stirring in presence of KOH pellets and consequently fractional distillation. For purification of compounds, the column chromatography was performed using 230-400 mesh silica gel (Merck).

II. Instrumentation and methodologies

II.1 NMR spectroscopy and mass spectrometry:

^{1}H NMR spectra were recorded for all synthesized compounds using Bruker 500 MHz spectrometer. 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. High resolution APCI mass spectra were collected using MicroTOF-Q-II spectrometer and $CHCl_3$ was used as eluent. Matrix assisted laser desorption/ ionization time of flight (MALDI-TOF) mass spectrometry was carried out using Bruker Daltonics UltrafleXtreme instrument and sinapinic acid was used as matrix.

II.2 Steady-state absorption and fluorescence measurement:

Steady-state absorption spectra for all derivatives in solution were recorded using Shimazu UV-Vis.-1800 spectrophotometer 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 concentration of all derivatives was maintained minimum to avoid the secondary inner filter effect. During the fluorescence measurement, both excitation and emission slits were kept as 1.5/ 1.5 nm. The absorption and emission studies were performed at room temperature (295 K).

II.3 Time-resolved fluorescence measurement:

Time-resolved fluorescence measurement was performed using time-correlated single photon counting (TCSPC) set up from Hamamatsu MCP Photomultiplier (R-3809U-50). For the excitation of molecule, 510 nm laser was used as excitation source 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 starting each measurement. The excitation and emission polarizer were fixed vertically and at magic angle (54.7 ^{o}) respectively. The decay curve was properly fitted using deconvolution method by EZtime software while keeping the fitting parameter χ^2 value in the range of 0.9-1.2. The fluorescence lifetime was measured at room temperature (295 K).

II.4 Electrochemical measurements:

Electrochemical or cyclic voltammetry measurements for all derivatives were performed using a CHI-6205 electrochemical analyzer instrument. Here, 0.1 M tetrabutyl ammoniumhexafluorophosphate (TBAP) was used as supporting electrolyte for each measurement and dye concentration was maintained as 0.05 mM. The measurements were done using three electrode configurations like Pt disk as working electrode, Pt wire as counter electrode and aqueous saturated Ag/ AgCl as reference electrode. Each dye and TBAP were taken in electrochemical cell and solubilized in dry DCM, then solution was purged with N_2 for 10-15 mins to remove the dissolved oxygen from solution. After that, all the voltammogram were recorded keeping the potential window -1.5 V to 1.5 V and the scan rate as 100 mV/ sec. Before starting every measurement, the working Pt disk electrode was polished on a felt pad with alumina powder and washed properly. All the measurements for each derivative were repeated for three times for better reproducibility.

II.5 Theoretical investigations:

The geometry optimizations of all compounds were performed with the D3BJ corrected B3LYP functional and def2-SVP basis set in gas-phase. The calculations of singlet excited state energies are carried out by adopting the TDDFT-Tamm-Dancoff approximation[1] alongwith range-separated CAM-B3LYP functional and def2-TZVP basis set. Those calculations are done at both gas-phase and polarized continuum model of toluene, chloroform and *N, N*-dimethyformamide (DMF) solvents. The calculations of emission wavelength are carried out at CAM-B3LYP/def2-SVP level in gas-phase. The possibilities of symmetry breaking CT phenomenon in *ortho*-, *meta*- and *para*-dimers are discussed with the calculated results in chloroform solvent. ORCA 5.0 program has been adopted for all of these calculations.[2] The natural transition orbital (NTO) files are generated with Multiwfn 3.8 program[3, 4] and drawn with Chemcraft 1.8[5] and VESTA[6] visualized software. The 3D scan of the dihedral angle between two PMI units in *ortho*-, *meta*- and *para*-dimers were performed with Gaussian 16 (G16) program. The scans are carried out from 0° to 90° with an interval of 10°. The coupling strengths between the interchromophoric HOMOs (J_{hh}), LUMOs (J_{ll}) and HOMO and LUMO (J_{hl}) are calculated

using the catnip tool.[7] The hole and electron transfer integrals (t_h and t_e) are calculated with the properties of interchromophoric HOMOs and LUMOs, respectively. The corresponding files are created with the G16 software.[8] The Coulomb electrostatic couplings (J_{Coul}) between two PMI units are estimated by using the calculated transition charges from electrostatic potential (TrESP). The TrESP and J_{Coul} both are calculated by using the G16[8] and Multiwfn 3.8 programs. All calculations are done at room temperature. The associated graphs are drawn by using origin 9.0 software.[9]

The internal reorganization energy (λ_i) is calculated by using,

$$\lambda_i = \left(E_{ES}^{-} - E_{GS}^{-}\right) + \left(E_{ES}^{+} - E_{GS}^{+}\right)$$

Where E_{ES} is the excited state optimized energy and E_{GS} is ground-state optimized energy, and (+) refers the cationic doublet state and (–) refers the anionic doublet state. Those are calculated by using the CAM-B3LYP functional and 6-31G basis set in ORCA. A two-sphere model that is based on the continuum solvent method is used to calculate the λ_s,[10]

$$\lambda_s = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{2r_A} + \frac{1}{2r_D} - \frac{1}{r_{DA}}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)$$

Therefore, λ_s depends upon the radii of the donor (r_D) and acceptor (r_A), the centre-to-centre distance between donor and acceptor (r_{DA}), and optical (ε_{op}) and static (ε_s) dielectric constant of the solvents. The r_D and r_A are calculated by using the cavity volume $\left(V = \frac{4}{3}\pi r^3\right)$ of the donor and acceptor, respectively.

Discussion on absorption and emission spectrum

The calculated absorption wavelengths $\left(\lambda_{abs}^{calc}\right)$ of PMI monomer, *ortho*-PMI dimer, *meta*-PMI dimer and *para*-PMI dimer are tabulated in Table S3. The results show negligible solvatochromism in the λ_{abs}^{calc} for all the compounds in toluene, chloroform and DMF solvents. Table S4 listed the energetically lowest four singlet excited states along with the involved transitions between the frontier molecular orbitals (FMOs). For *ortho*-PMI dimer, both S_1 and S_2 states are the optically active states with an oscillator strength of 1.16 and 2.11, respectively. The larger oscillator strength corresponding to the $S_2 \leftarrow S_0$ transition provide a conformation of the absorption and this finding corroborate with the ratio of intensities from experiment $\left(\frac{A_{0\leftarrow0}}{A_{1\leftarrow0}} < 1\right)$. For both *meta*-PMI and *para*-PMI dimers, the oscillator strength for $S_1 \leftarrow S_0$ transition are 2.58 and 3.84, respectively, which are also in agreement with the

experiment $\left(\frac{A_{0\leftarrow 0}}{A_{1\leftarrow 0}} > 1\right)$. The H – 1 → L and H → L+1 transitions are providing the major contribution in $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ excitations of *ortho*-PMI and *meta*-PMI dimer, respectively, whereas a H→L transition is involved with the $S_1 \leftarrow S_0$ excitation in *para*-PMI dimer. The finding can explain the reason of a bathochromic shift in the absorption band of *para*-PMI dimer compared to the *ortho*-PMI and *meta*-PMI dimers (Table S3). The emission wavelengths (λ_{em}^{calc}) and the corresponding oscillator strengths are provided in Table S5. The Stokes shift $\left(\lambda_{S_1 \rightarrow S_0} - \lambda_{S_1 \leftarrow S_0}\right)$ in *ortho*-PMI dimer is similar with that of in PMI monomer, 35 and 31 nm, respectively, indicates a possibility of excitonic communication in the excited states. A prominent charge-transfer between the PMI units of *ortho*-PMI dimer is captured in the S_3 and S_4 excited states with oscillator strengths of 0.00 and 0.01, respectively. The S_3 and S_4 sates are 0.04 eV apart from each other and they are together designated as a CT-like or charge-resonance excitons as the hole and electron wavefunctions are interchanging in these two states (Table S4). The natural transition orbital (NTO) plots are shown in the **Fig. S33** along with the isosurface plots of FMOs. A negligible CT-like behavior is identified in the S_3 and S_4 states of *meta*-PMI dimer whereas no CT-like behavior is not observed among those states of *para*-PMI dimer. Herein, we refer to the bond length alternation (BLA) value of the phenyl spacer (sPh), which is the difference between the average length of even bonds and that of odd bonds. The BLA value of the sPh in the *ortho*-PMI dimer is estimated as –0.004Å while the values are 0.000Å and 0.001Å for the *meta*-PMI and *para*-PMI dimers, respectively. Hence, the possibility of formation of zwitterionic structure (quinoid =Ph=) of *ortho*-PMI dimer is more significant in the ground state than the others, which provide a spontaneity in the generation of CT-like state.

A description on J and H aggregation:

In dimer approach, a dimer consists with two monomeric units *M* and two configurations of Frenkel and charge separated (CS) excitations are possible ($|MM^*\rangle$ and $|M^*M\rangle$) and ($|M^-M^+\rangle$ and $|M^+M^-\rangle$), respectively. These degenerate states are designated as localized Frenkel and CS excitations that residing on the monomer units.[11] The interaction between the localized Frenkel states results in a splitting of $\langle MM^* \,|\, M^*M\rangle$ and creates two delocalized Frenkel (DF) states $\frac{1}{\sqrt{2}}\left(|MM^*\rangle - |M^*M\rangle\right)$ and $\frac{1}{\sqrt{2}}\left(|MM^*\rangle + |M^*M\rangle\right)$. The first DF (antisymmetric) state is stabilized by $-J_{Coulomb}$ and the second DF (symmetric) state is destabilized by $+J_{Coulomb}$, which gives a resultant splitting parameter $+2J_{Coul}$.[12] This is a sign of H-aggregation ($J_{Coul} > 0$) while the ordering is reversed in case of J-aggregation ($J_{Coul} < 0$). Hence, the transition dipole moment corresponding to the absorption at the symmetric (higher

energy) state is larger than the monomeric transition dipole in H-aggregation.[12] The illustration of this mechanism is shown in **Fig. 3a-c** of the manuscript.

II.6 Femtosecond transient absorption study (fs-TAS):

A detailed discussion about the current experimental setup for the transient absorption measurements can be found elsewhere.[13, 14] Briefly, 530 nm (for monomer, *ortho*-, *meta*-, *para*-dimers and 1,3,5- trimer) and 550 nm (for self-coupled dimer) laser pulses are used as the excitation source and a broadband white light probe pulse, generated by a non-linear CaF_2 crystal is used to investigate the pump-induced changes in the sample over delay times, in a custom-made femtosecond transient absorption spectrometer where the angle between polarization vectors of pump and probe pulses is kept at magic angle (54.7°) to negate molecular anisotropies. The pump and probe beams are focused and crossed in a 1 mm path length sample quartz cuvette. Differential absorption spectra are collected by varying the pump-probe time delay keeping 1 sec integration time (*i.e.*, averaging over 1000 laser shots). For transient absorption spectra, the optically-induced change in the sample is described as the pump-induced absorption changes of the probe beam, where $\Delta A < 0$ represents ground state bleaching (GSB)/stimulated emission (SE) and $\Delta A > 0$ represents excited state absorption (ESA). Data are collected at three segments with different step-sizes (-1 ps to 1/ 0.01 ps, 1 ps to 100 ps/ 0.5 ps and 100 ps to 3.7 ns/5 ps) and subsequently joined for further analysis. All the measurements are carried out at room temperature (298 K), and no photo degradation of the samples is noticed after the pump-probe measurements.

Global and target analysis of fs-TA data

To extract the ultrafast charge separation (CS) and charge recombination (CR) time constants of dimers and trimer in solvents with different polarity, the data is analyzed globally, TA data is analyzed globally to fit it with the singular value decomposition factors in the using a free R-package TIMP software with the graphical interface program Glotaran (version 1.5.1) software. Based on the statistical fitting package TIMP, we have analyzed TA data using a kinetic model (global and target analysis) [3-4]. Singular value decomposition (SVD) was performed on TA data set matrix ΔA (t, λ) to determine the number of major components that should be fitted to in the global analysis. SVD calculations showed that the data set had at least four significant components. The transient absorption spectra are globally fitted by considering a consecutive sequential relaxation model and the associated spectra are called evolution associated difference spectra (EADS) are obtained, which can be described as follows:

Where,

$$c_{i}^{EADS}(t) = \sum_{j=1}^{i} b_{ij} \exp(-k_j t) \oplus i(t)$$

$$b_{ij} = \prod_{m=1}^{i} k_m \Big/ \prod_{n=1,\, n \neq j}^{i} (k_n - k_j)$$

i(t) is the instrument response function (IRF), k_j is the decay rate of component j and the amplitude b_{ji} of the exponential decay is defined for $j \leq I$ assuming $b_{11} = 1$.

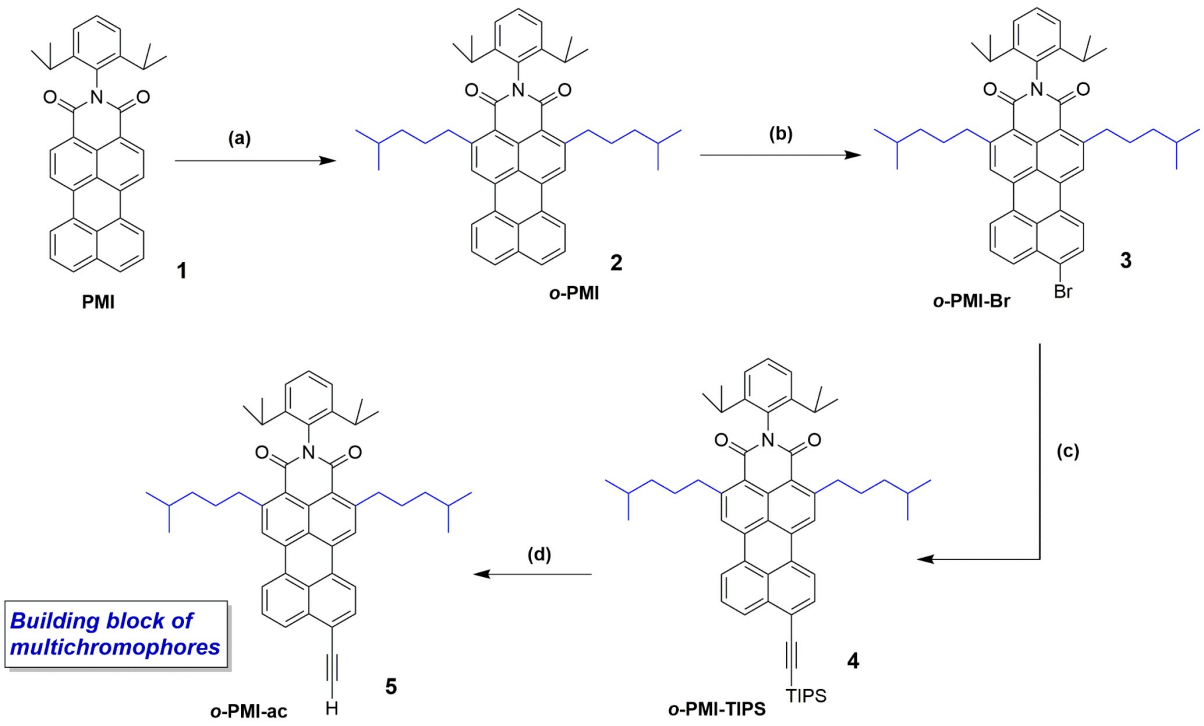
We obtained (from global analysis) sequentially interconverting evolution associated difference spectra (EADS), *e.g.*, 1 → 2 → 3…; where the arrows indicate successive mono-exponential decays of increasing time constants, which can be regarded as the lifetime of each EADS. This procedure validates a depiction of the evolution of the (excited) states of the system. For obtaining the contributions from these molecular species (because the EADS may reflect mixtures of molecular species), a target analysis was performed in which a specific kinetic scheme was applied. We obtained the spectrum signature of the "pure" excited and product state intermediates as species-associated difference spectra (SADS). Each of these states can be ascribed to a distinct intermediate of the relaxation process. Further, Matlab programming (Matlab2019a, MathWorks) software is used to plot the figures.

For analyzing the TA signals at the probe wavelength 590 nm corresponding to radical cation absorption, kinetic traces are fitted with a custom equation (Equation 1) [3].

$$Y(t,\mu,t_i,\sigma) = \sum_{i=1}^{n} \frac{a_i}{2} e^{\left(\frac{1}{2\tau_1}\left(\frac{\sigma^2}{\tau_i} - 2(t-u)\right)\right)} \left[1 - erf\left(\frac{\sigma^2 - \tau_i(t-u)}{\sigma\sqrt{2}\,\tau_i}\right)\right] \quad (1)$$

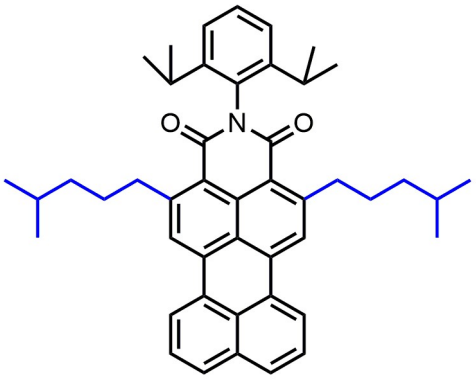
σ and μ are the standard deviation and mean position of Gaussian instrument response function IRF, $\tau_i{}'s$ are the time constants for the exponential decays.

III. Synthetic procedures and characterizations:



(a) 4-Methyl-1-pentene, $Ru(CO)(H)_2(PPh_3)_3$, anhydrous mesitylene, 145 °C, 48 h, 56%; (b) Br_2, DCM, 52 °C, 2 h, 76%;
(c) (Triisopropylsilyl)acetylene, $Pd_2(dba)_3$, P(*o*-tolyl)$_3$, Toluene:TEA (5:1), 65 °C,18 h, 89%, (d) TBAF, anhydrous THF, RT, 45 mins, 87%

Scheme S1: Synthetic route for preparation of ***o*-PMI-ac** monomer.

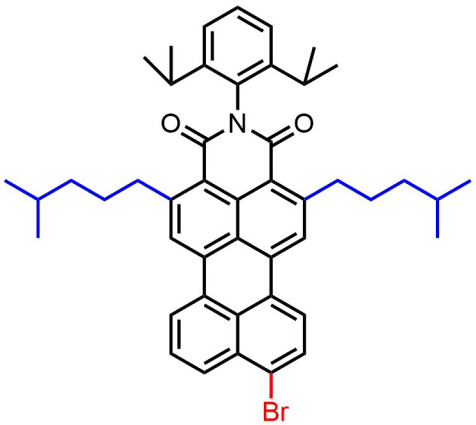


Synthesis of compound 2: In a 5 mL microwave vial, compound **1** (100 mg, 0.207 mmol) and the catalyst $Ru(CO)(H)_2(PPh_3)_3$ (31.5 mg, 0.0342 mmol) were taken and the vial was properly sealed. Then, inert atmosphere was created inside the vial by several round of gassing-degassing cycle for few minutes. Anhydrous mesitylene (3.5 mL) followed by 4-methyl-1-pentene (660 μL, 5.176 mmol) was added in the solid reaction mixture. Then the solution was bubbled with N_2 for 30 mins at room temperature (RT) along with stirring using N_2–filled balloon. Finally, the reaction mixture was kept on stirring at 145 °C for 72 h and the reaction mixture showed a color change. After completion of reaction,

the solution was cooled down to RT and MeOH was added in the reaction mixture. Instantly, orange precipitate was formed in the solution. The solution was filtered, residue was properly dried and collected. The crude product was purified by column chromatography using distilled $CHCl_3$ as eluent. The desired compound **2** was obtained as pure bright orange colored solid (76 mg), yield – 56%.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.50 (d, J = 7.5 Hz, 1H), 8.27 (s, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.67 (t, J = 7.8 Hz, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 3.50 – 3.46 (m, 4H), 2.81 – 2.75 (m, 2H), 1.75 – 1.69 (m, 4H), 1.52 (d, J = 6.8 Hz, 2H), 1.38 – 1.34 (m, 4H), 1.18 (d, J = 6.9 Hz, 12H), 0.85 (d, J = 6.6 Hz, 12H).

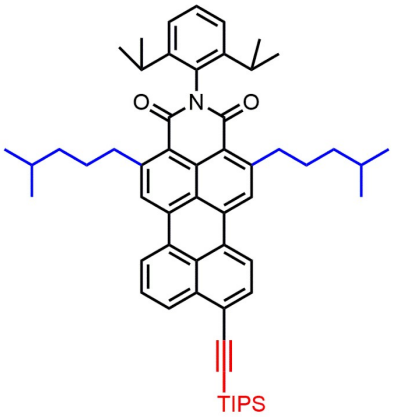
Chemical Formula – $C_{46}H_{51}NO_2$ **Calculated mass** - 649.392 and **obtained mass** – 650.400 $[M+H]^+$. This mass data is determined using APCI technique.



Synthesis of compound 3: In a 100 mL RB flask, compound **2** (274 mg, 0.422) was dissolved in distilled DCM (35 mL) under stirring condition. Bromine (45 μL) solution was dropwise added in the stirring reaction mixture. The final reaction mixture was transferred on a heating bath and refluxed for 2 h. After completion of reaction, bromine and DCM were removed under lower pressure. The crude was purified by column chromatography using distilled $CHCl_3$ as eluent. The compound obtained after column chromatography was further purified by precipitation using MeOH-$CHCl_3$ solvent mixture to afford the title compound as orange solid product (232.4 mg), yield – 76%.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.55 (d, J = 7.4 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.31 (s, 1H), 8.29 (d, J = 5.2 Hz, 1H), 8.24 (s, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.37 (d, J = 7.8 Hz, 2H), 3.50 (m, 4H), 2.81 (m, 2H), 1.74 (m, 4H), 1.55 (m, 2H), 1.39 (m, 4H), 1.21 (d, J = 6.8 Hz, 12H), 0.87 (m, 12H).

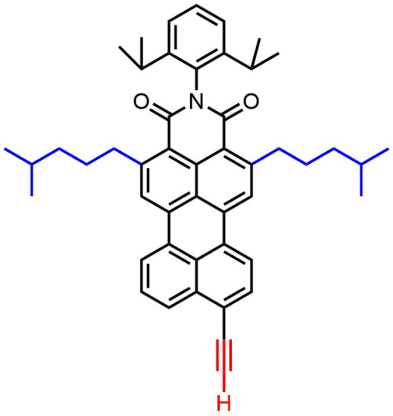
Chemical Formula – $C_{46}H_{50}BrNO_2$ **Calculated mass** -727.3025 and **obtained mass** – 728.312 $[M+H]^+$. This mass data is determined using APCI technique.



Synthesis of compound 4: In a schlenk tube, compound **3** (300 mg, 0.411 mmol) was taken and charged under N_2 atmosphere. Anhydrous toluene (7.5 mL) and triethylamine (1.5 mL) were added in the Schlenk tube having compound **3** in presence of continuous N_2 flow. (Triisopropylsilyl)acetylene (600 μL, 2.678 mmol) was consequently added in the solution. Then, the solution was kept in liquid N_2 to freeze and vacuum was applied. The Schlenk tube containing frozen solid mixture was taken out from liquid N_2 and come to RT by heating. The liquefied solution was stirred for 3 mins constantly at RT for proper mixing. Again, the Schlenk tube was transferred in liquid N_2 and same process was done for 3-4 times. After that, in frozen mixture, the catalyst $Pd_2(dba)_3$ (38 mg, 0.0414 mmol) and ligand P(*o*-tol)$_3$ (97.3 mg, 0.267 mmol) were added under N_2 atmosphere. Again, the above-mentioned gassing-degassing process (freeze-pump-thaw method) was repeated for several times. Finally, the liquefied solution was transferred on a heating bath and stirred at 65 ^oC for 18 h under inert atmosphere. When reaction was completed, the solvents were evaporated under lower pressure. The crude was dissolved in distilled $CHCl_3$, mixed with silica gel and purified by column chromatography using $CHCl_3$ as eluent to afford desired compound. Further, precipitation was done with MeOH-$CHCl_3$ to afford title compound (310 mg) as pure orange solid, yield – 89%.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.51 (dd, J = 21.6, 7.9 Hz, 2H), 8.40 (d, J = 7.9 Hz, 1H), 8.27 (s, 1H), 8.23 (s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 3.48 (m, J = 7.8 Hz, 4H), 2.77 (m, J = 6.9 Hz, 2H), 1.71 (m, J = 11.3, 9.6, 5.8 Hz, 4H), 1.53 (d, J = 6.6 Hz, 2H), 1.36 (q, J = 7.2 Hz, 4H), 1.23 (m, 21H), 1.18 (d, J = 6.8 Hz, 12H), 0.85 (d, J = 6.6 Hz, 12H).

Chemical formula – $C_{57}H_{71}NO_2Si$ **Calculated mass** – 829.525 and **obtained mass** – *m/z* 830.533 $[M+H]^+$. This mass data is determined using APCI technique.



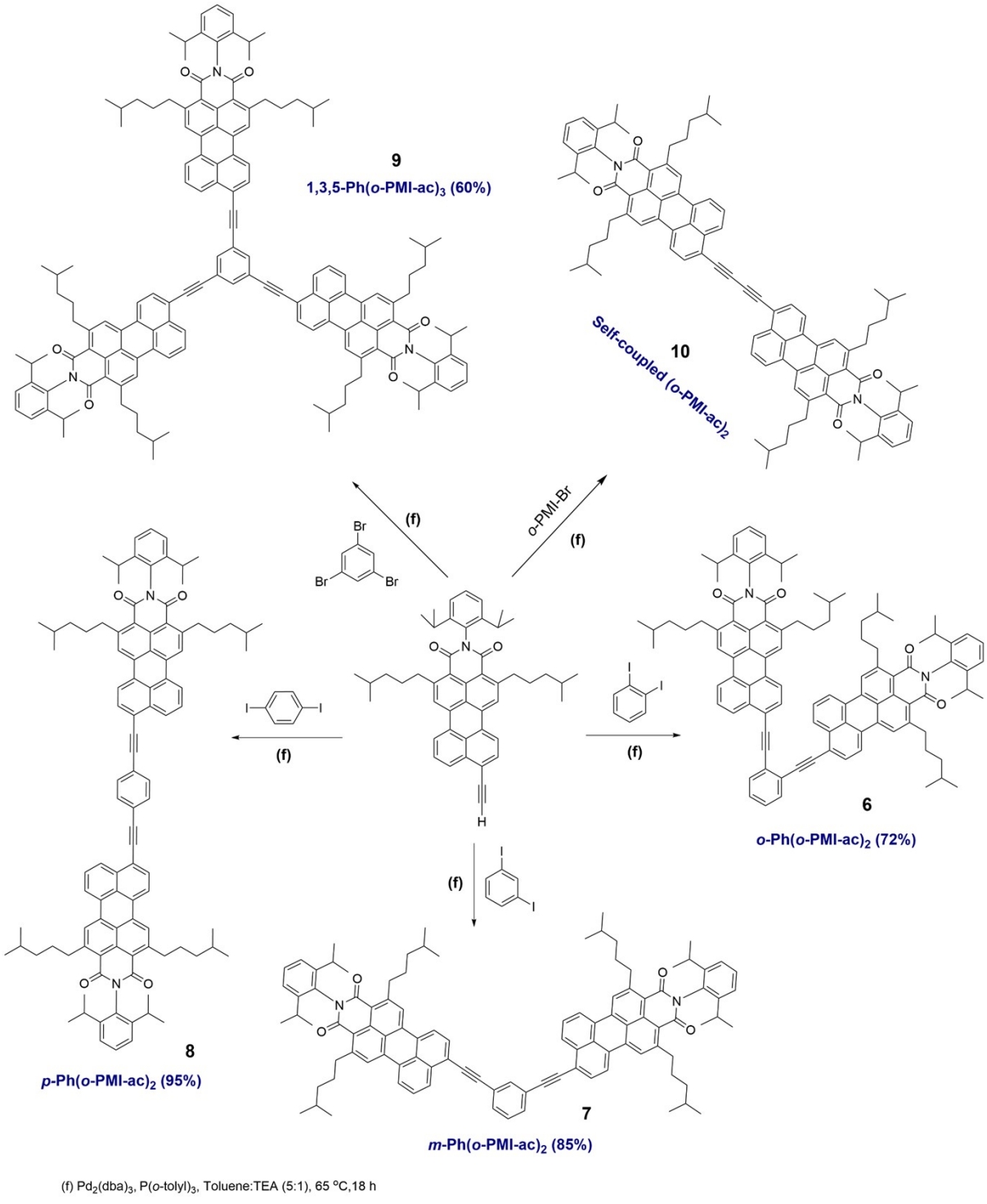
Synthesis of compound 5: In 25 mL RB flask, compound **4** (100 mg, 0.118 mmol) was dissolved in anhydrous THF (10 mL) in presence of N_2 atmosphere. The reaction mixture was kept on ice bath and stirred for 5 mins at RT to dissolve the compound completely. Then, TBAF (85 μL, 0.354 mmol) solution was dropwise added in the above solution under N_2 atmosphere. The reaction mixture was stirred at same temperature for 1 h. Distilled water was poured in the reaction mixture to capture tetrabutylammonium cation (TBA^+) and precipitate was formed at the bottom of the solution. After filtering the solution, the crude was purified by column chromatography using $CHCl_3$ as eluent. The collected compound was precipitated using MeOH-$CHCl_3$ solvent mixture to get pure solid-orange product (70 mg), yield – 87%.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.53 (d, J = 7.0 Hz, 1H), 8.44 (dd, J = 8.3, 7.3 Hz, 2H), 8.27 (s, 1H), 8.24 (s, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.75 (dd, J = 8.4, 7.5 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 3.67 (s, 1H), 3.48 (dt, J = 7.9, 3.9 Hz, 4H), 2.78 (m, J = 6.8 Hz, 2H), 1.71 (m, J = 9.1 Hz, 4H), 1.51 (t, J = 1.1 Hz, 2H), 1.36 (dd, J = 8.1, 2.3 Hz, 4H), 1.19 (d, J = 6.9 Hz, 12H), 0.85 (d, J = 5.9 Hz, 12H).

Chemical formula – $C_{48}H_{51}NO_2$ **Calculated mass** – 673.392 and **obtained mass** – *m/z* 674.398 $[M+H]^+$. This mass data is determined using APCI technique.

Synthesis of compound 6, 7, and 8: The *ortho*-PMI dimer/ ***o*-Ph(*o*-PMI-ac)$_2$** (**6**), *meta*-PMI dimer/ ***m*-Ph(*o*-PMI-ac)$_2$** (**7**) and *para*-PMI dimer/ ***p*-Ph(*o*-PMI-ac)$_2$** (**8**) were synthesized by following same synthetic protocol mentioned below but their purification techniques were slightly different.

In a Schlenk tube, 1,2-diiodobenzene (4 μL, 0.0303 mmol)/ 1,3-diiodobenzene (10 mg, 0.0303 mmol)/ 1,4-diiodobenzene (10 mg, 0.0303 mmol) and compound **5** (45 mg, 0.0667 mmol) were taken together and the Schlenk RB was charged under N_2 atmosphere. Anhydrous toluene (6 mL) and triethylamine (1.2 mL) were subsequently added in the reaction mixture in presence of N_2 atmosphere. Then the



Scheme S2: Synthesis of regioisomeric derivatives.

solution was transferred into liquid N_2 solution to freeze. After freezing completely, vacuum and N_2 were applied repeatedly for 4-5 times. The frozen reaction mixture was taken out in presence of N_2 from liquid N_2 and come to RT by applying heat. The liquefied reaction mixture was stirred at RT for 3 mins to dissolve the compounds completely. Again, the solution was kept in liquid N_2 and repetitive vacuum/ N_2 cycles were carried out. The same freeze-pump-thaw process was repeated for several

times. In frozen mixture, the catalyst $Pd_2(dba)_3$ (7.1 mg, 0.007 mmol) and ligand P(*o*-tol)$_3$ (17 mg, 0.0466 mmol) were added under N_2 atmosphere. Again, the above-mentioned gassing-degassing process was done for three times. Finally, the reaction mixture was transferred on a heating bath and stirred at 65 ^oC for 18 h under inert atmosphere.

Purification: After reaction was completed, the solvents were removed under low pressure and crude mixture was purified by column chromatography using silica gel. For *meta*-PMI dimer (**7**) and *para*-PMI dimer (**8**), eluent was used a 2:1 solvent mixture of $CHCl_3$ and hexane. Compound *meta*-dimer (**7**) and *para*-dimer (**8**) were obtained as 37 mg (yield – 86%) and 41 mg (yield - 95%) respectively. On the other hand, the crude of *ortho*-PMI dimer (**6**) was purified using a different solvent mixture of ethyl acetate and hexane (1:19 ratio) and the compound was afforded as 31 mg (yield – 72%).

^{1}H NMR (500 MHz, Chloroform-*d*):

***o*-Ph-(*o*-PMI-ac)$_2$ (6):** δ 8.66 (d, J = 8.1 Hz, 2H), 8.47 (d, J = 8.0 Hz, 2H), 8.38 (d, J = 7.3 Hz, 2H), 8.27 (s, 2H), 8.20 (s, 2H), 7.98 (d, J = 7.9 Hz, 2H), 7.82 (dd, J = 5.8, 3.3 Hz, 2H), 7.50 (dd, J = 5.8, 3.3 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.9 Hz, 4H), 7.24 (t, J = 7.9 Hz, 2H), 3.46 (dt, J = 20.6, 7.8 Hz, 8H), 2.77 (m, 4H), 1.70 (m, 8H), 1.50 (dt, J = 13.4, 6.7 Hz, 4H), 1.34 (m, 8H), 1.18 (dd, J = 6.9, 1.8 Hz, 24H), 0.82 (dd, J = 12.0, 6.6 Hz, 24H).

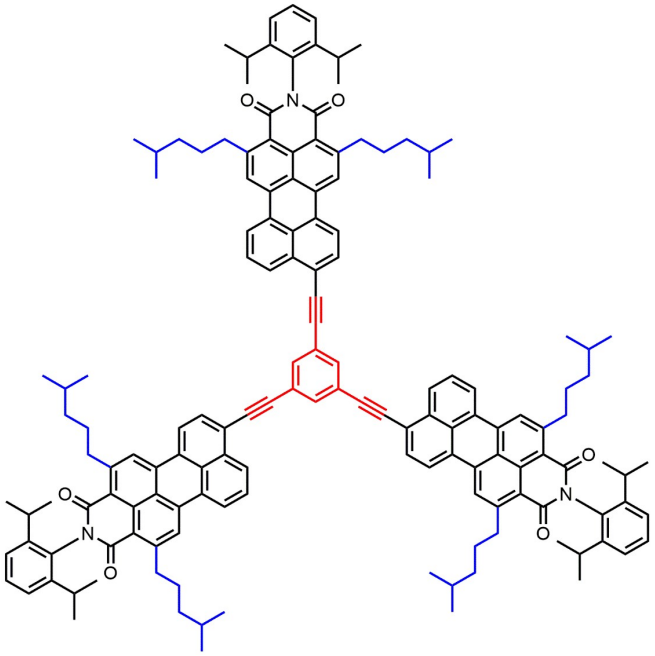
Chemical formula – $C_{102}H_{104}N_2O_4$ **Calculated mass** – 1421.803 and **obtained mass** – *m/z* 1421.805 $[M]^+$. This mass data is determined using APCI technique.

***m*-Ph-(*o*-PMI-ac)$_2$ (7):** δ 8.57 (dd, J = 3.7 Hz, 4H), 8.49 (d, J = 8.1 Hz, 2H), 8.30 (s, 2H), 8.20 (s, 2H), 8.03 (s, 1H), 7.94 (d, J = 7.9 Hz, 2H), 7.82 (t, J = 7.9 Hz, 2H), 7.74 (dd, J = 7.7, 1.7 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.47 (t, J = 7.3 Hz, 2H), 7.35 (d, J = 7.9 Hz, 4H), 3.50 (t, J = 7.8 Hz, 8H), 2.79 (m, 4H), 1.73 (m, 8H), 1.37 (q, J = 7.2 Hz, 8H), 1.19 (d, J = 6.8 Hz, 24H), 0.86 (dd, J = 5.3 Hz, 24H).

Chemical formula – $C_{102}H_{104}N_2O_4$ **Calculated mass** – 1421.803 and **obtained mass** – *m/z* 1421.804 $[M]^+$. This mass data is determined using APCI technique.

***p*-Ph-(*o*-PMI-ac)$_2$ (8):** δ 8.57 (dd, J = 13.7, 7.9 Hz, 4H), 8.49 (d, J = 8.1 Hz, 2H), 8.31 (s, 2H), 8.29 (s, 2H), 7.94 (d, J = 7.7 Hz, 2H), 7.81 (t, J = 7.9 Hz, 2H), 7.76 (s, 4H), 7.47 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 4H), 3.50 (t, J = 7.8 Hz, 8H), 2.79 (m, 4H), 1.72 (m, 8H), 1.51 (t, 4H), 1.37 (q, J = 7.3 Hz, 8H), 1.19 (d, J = 6.8 Hz, 24H), 0.86 (d, J = 6.6 Hz, 24H).

Chemical formula – $C_{102}H_{104}N_2O_4$ **Calculated mass** – 1421.803 and **obtained mass** – *m/z* 1422.808 $[M+H]^+$. This mass data is determined using APCI technique.



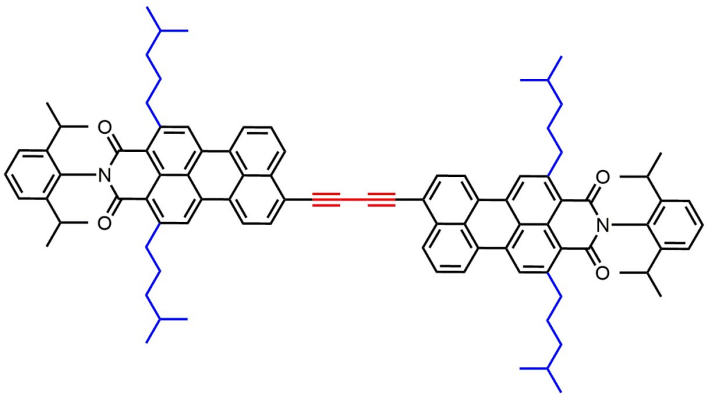
Synthesis of 1,3,5-Ph(*o*-PMI-ac)$_3$ (9): For the synthesis of compound **9**, the synthetic protocol was followed same as mentioned for **6**, **7**, and **8**. But, the reagents were taken in different amount as mentioned below.

(a) 1,3,5-tribromo benzene – 5.4 mg, 0.0171 mmol (b) *o*-PMI-acetylene (**4**) – 36.4 mg, 0.054 mmol, (c) $Pd_2(dba)_3$ – 5.4 mg, 0.0059 mmol (d) P(*o*-tol)$_3$ – 13 mg, 0.0356 mmol; anhydrous toluene – 4 mL and anhydrous triethylamine – 0.8 mL.

The crude was purified by column chromatography using 2:1 solvent mixture of $CHCl_3$ and hexane as eluent to afford the title compound as 21.5 mg, yield – 60%.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.60 (d, J = 8.0 Hz, 6H), 8.51 (d, J = 8.1 Hz, 3H), 8.31 (d, J = 6.6 Hz, 6H), 8.04 (s, 3H), 7.98 (d, J = 7.8 Hz, 3H), 7.86 (t, J = 8.0 Hz, 3H), 7.47 (t, J = 7.9 Hz, 3H), 7.36 (d, J = 7.8 Hz, 6H), 3.50 (t, J = 7.7 Hz, 12H), 2.80 (m, 6H), 1.73 (m, 12H), 1.51 (t, 6H), 1.38 (q, J = 6.4, 6.0 Hz, 12H), 1.20 (d, J = 6.9 Hz, 36H), 0.86 (dd, J = 6.6, 2.2 Hz, 36H).

Chemical formula – $C_{150}H_{153}N_3O_6$ **Calculated mass** –2094.183 and **obtained mass** – *m/z* 2094.933. This mass data is determined using MALDI technique.



Synthesis of self-coupled (*o*-PMI-ac)$_2$ (10): Compound **10** was obtained as a side-product of reaction between ***o*-PMI-ac** (10.65 mg, 0.0158 mmol) and ***o*-PMI-Br** (10.5 mg, 0.0144 mmol) using the same catalytic system and mixture of anhydrous toluene and TEA (5:1 ratio) solvent. The desired compound **(*o*-PMI)$_2$-ac** was not separated after repetitive column chromatography. Instead of that, the abovementioned self-coupled derivative was afforded as major product as 14.0 mg, yield – 72%.

^{1}H NMR (500 MHz, Chloroform-*d*) of Compound (10): δ 8.57 (d, J = 7.6 Hz, 2H), 8.52 (d, J = 8.4 Hz, 2H), 8.47 (d, J = 8.1 Hz, 2H), 8.30 (s, 2H), 8.28 (s, 2H), 7.98 (d, 2H), 7.82 (t, 2H), 7.47 (m, 2H), 7.36 (d, 4H), 3.51 (t, J = 7.6 Hz, 8H), 2.79 (m, 4H), 1.73 (m, 8H), 1.54 (t, 4H), 1.38 (m, 8H), 1.20 (d, J = 6.9 Hz, 24H), 0.86 (d, J = 6.6 Hz, 24H).

Chemical formula – $C_{96}H_{100}N_2O_4$ **Calculated mass** –1345.772 and **obtained mass** – *m/z* 1345.777 $[M]^+$. This mass data is determined using APCI technique.

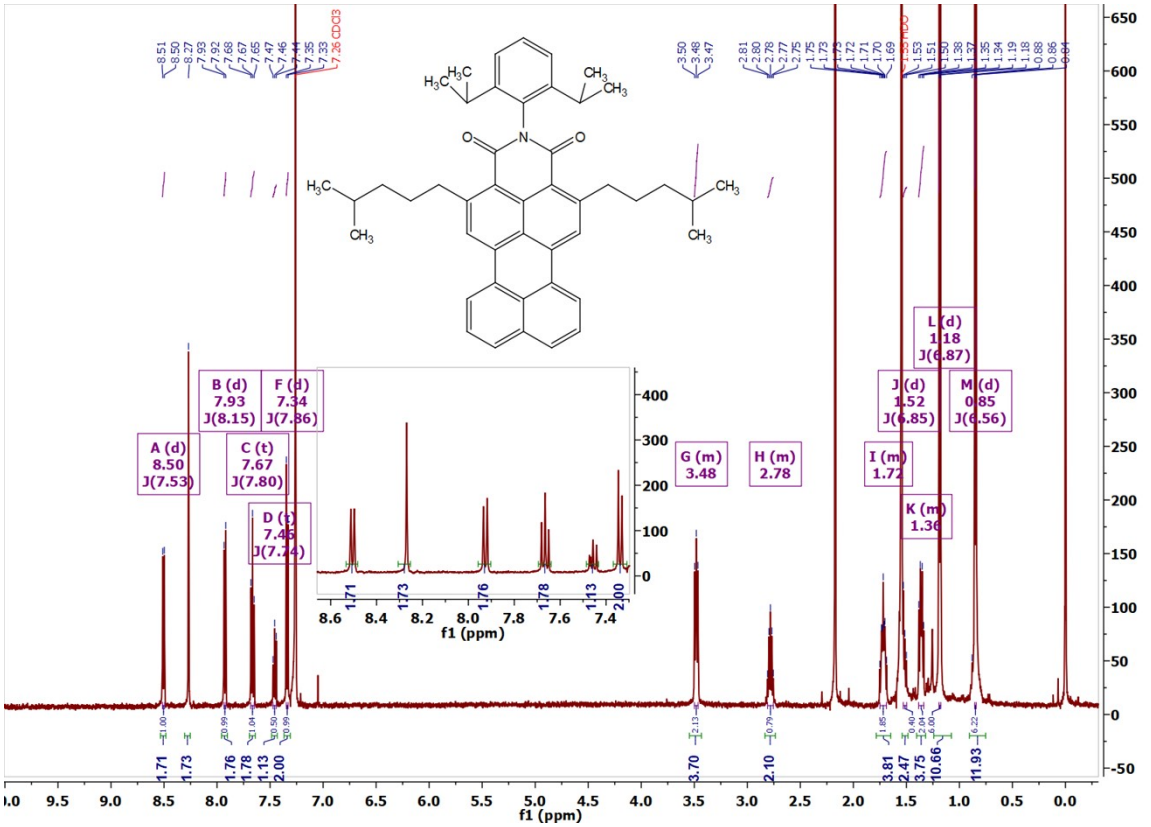


Fig. S1 ^{1}H NMR spectrum of ***o*-PMI (2)** in $CDCl_3$ at 500 MHz.

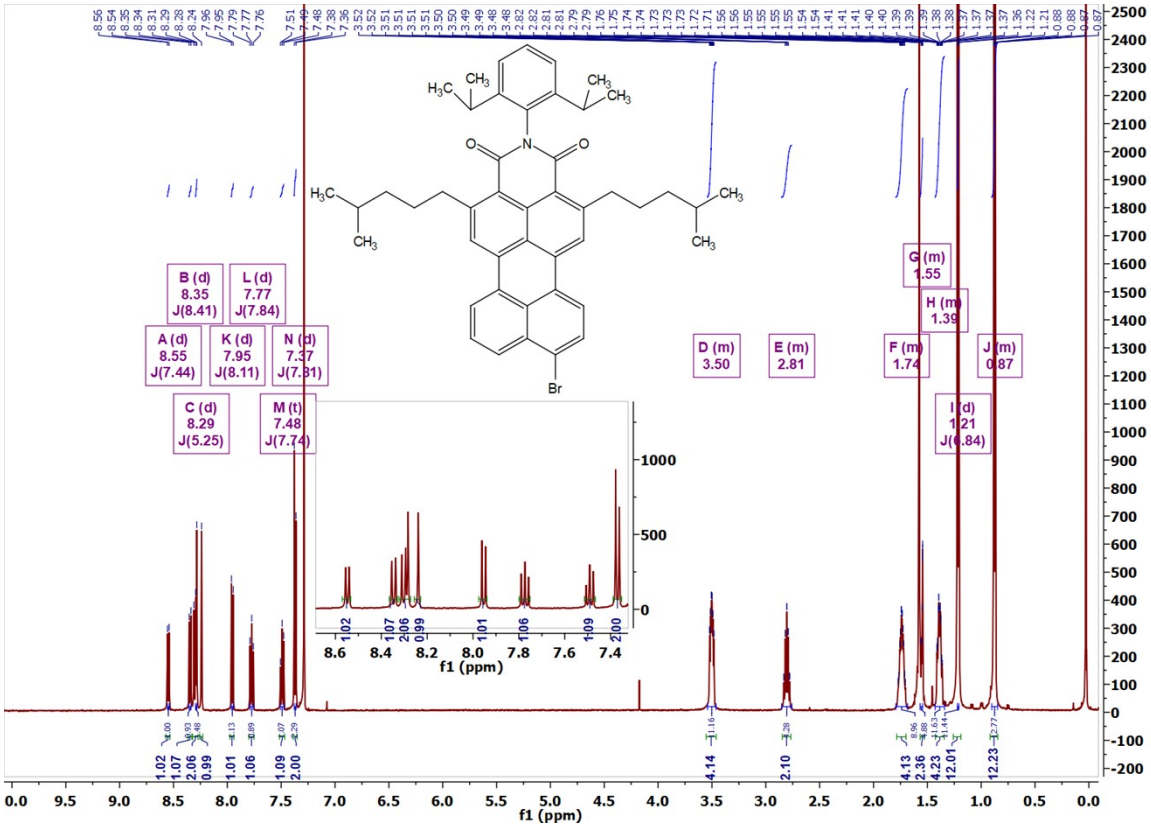


Fig. S2 ^{1}H NMR spectrum of ***o*-PMI-Br (3)** in $CDCl_3$ at 500 MHz.

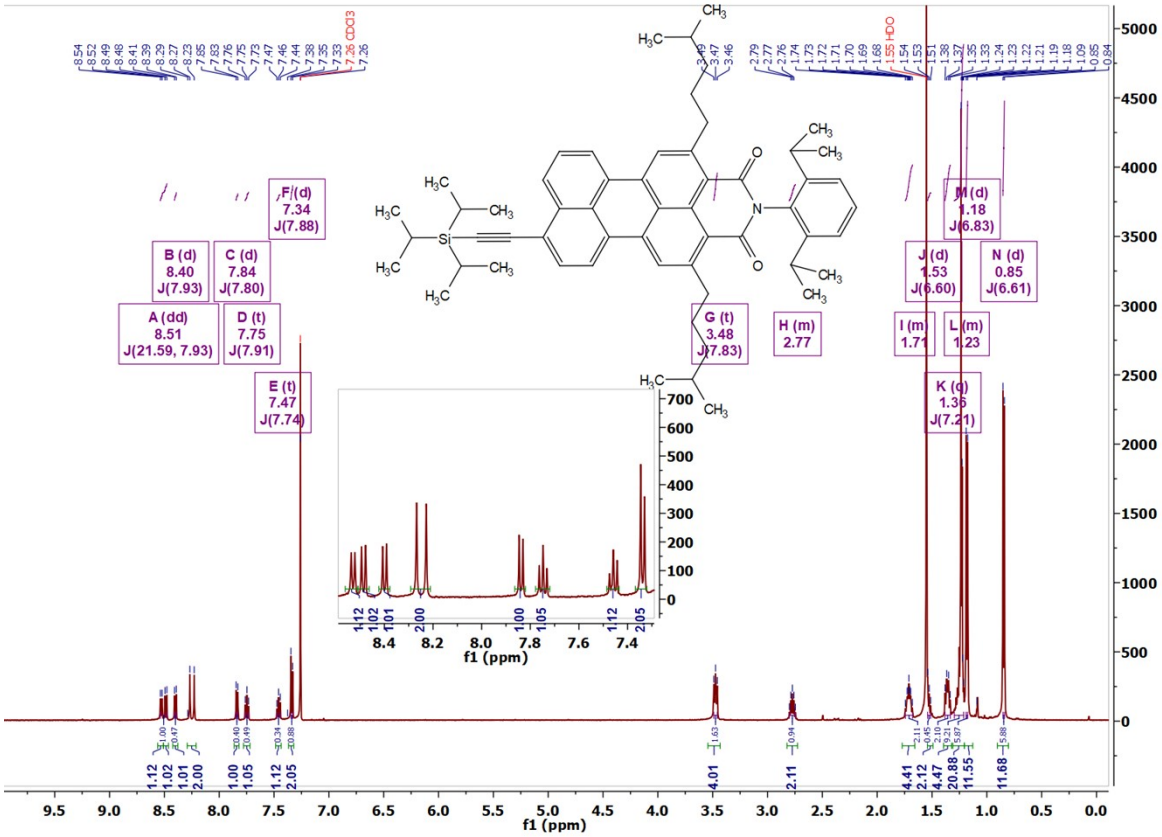


Fig. S3 ^{1}H NMR spectrum of ***o*-PMI-TIPS (4)** in $CDCl_3$ at 500 MHz.

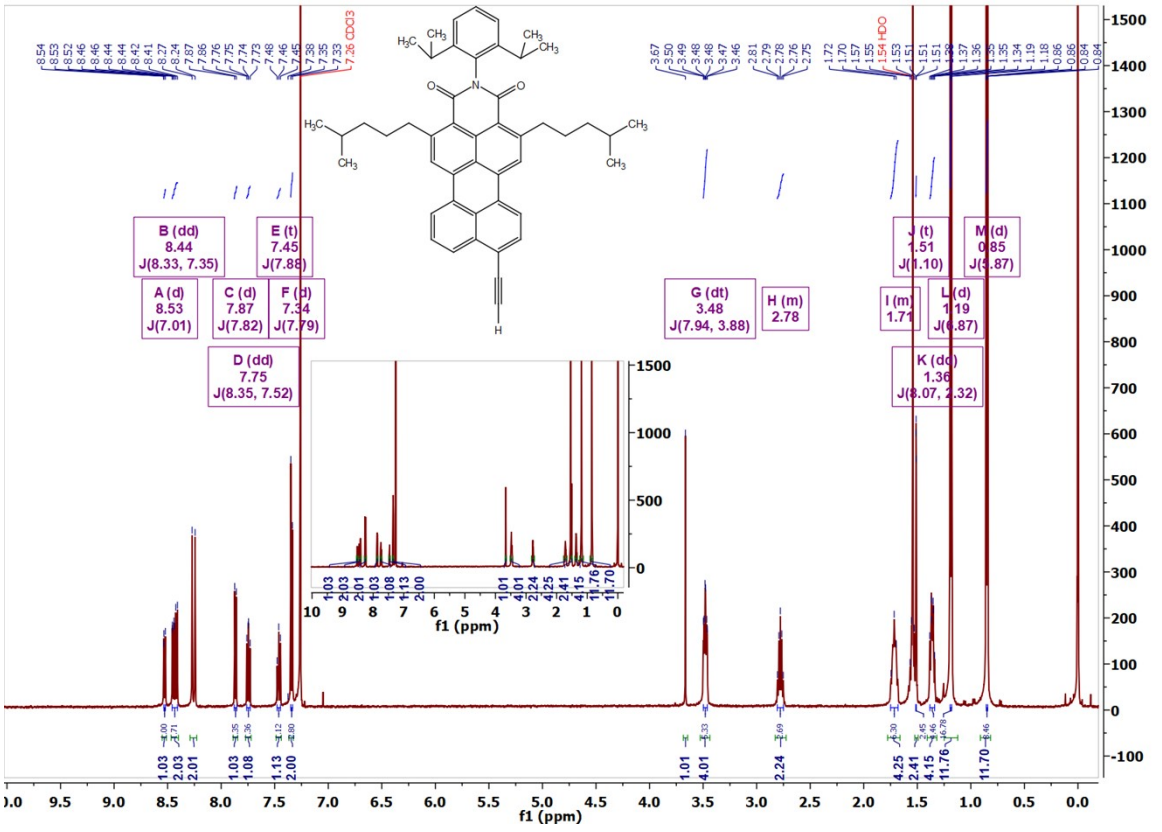


Fig. S4 ^{1}H NMR spectrum of ***o*-PMI-ac (5)** in $CDCl_3$ at 500 MHz.

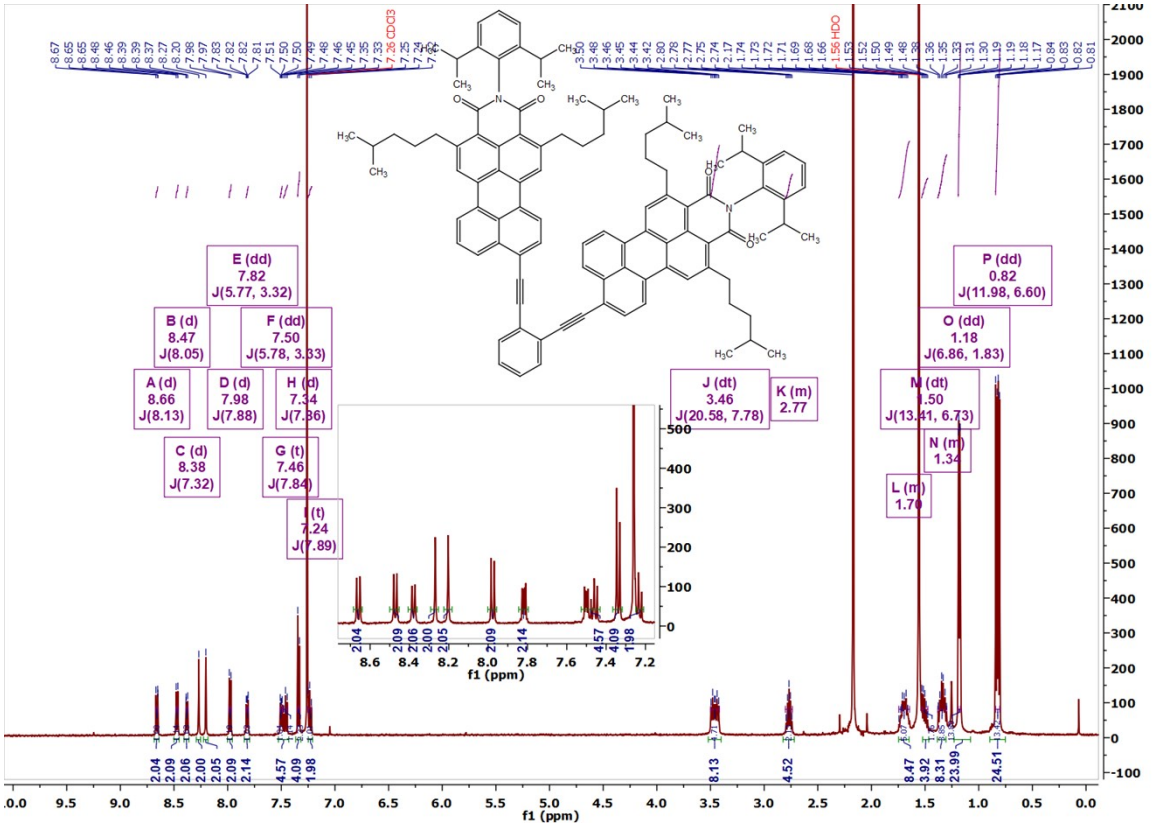


Fig. S5 ^{1}H NMR spectrum of ***o*-Ph(*o*-PMI-ac)$_2$** in $CDCl_3$ at 500 MHz.

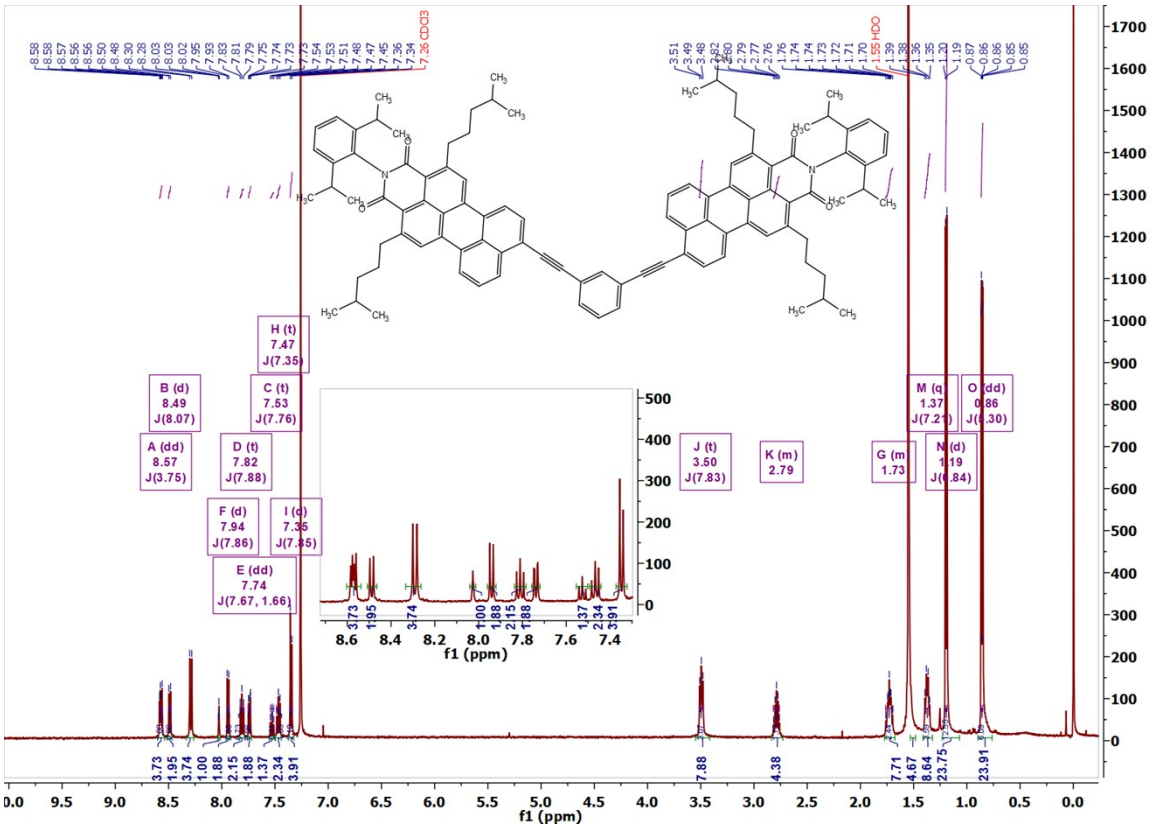


Fig. S6 ^{1}H NMR spectrum of ***m*-Ph(*o*-PMI-ac)$_2$** in $CDCl_3$ at 500 MHz.

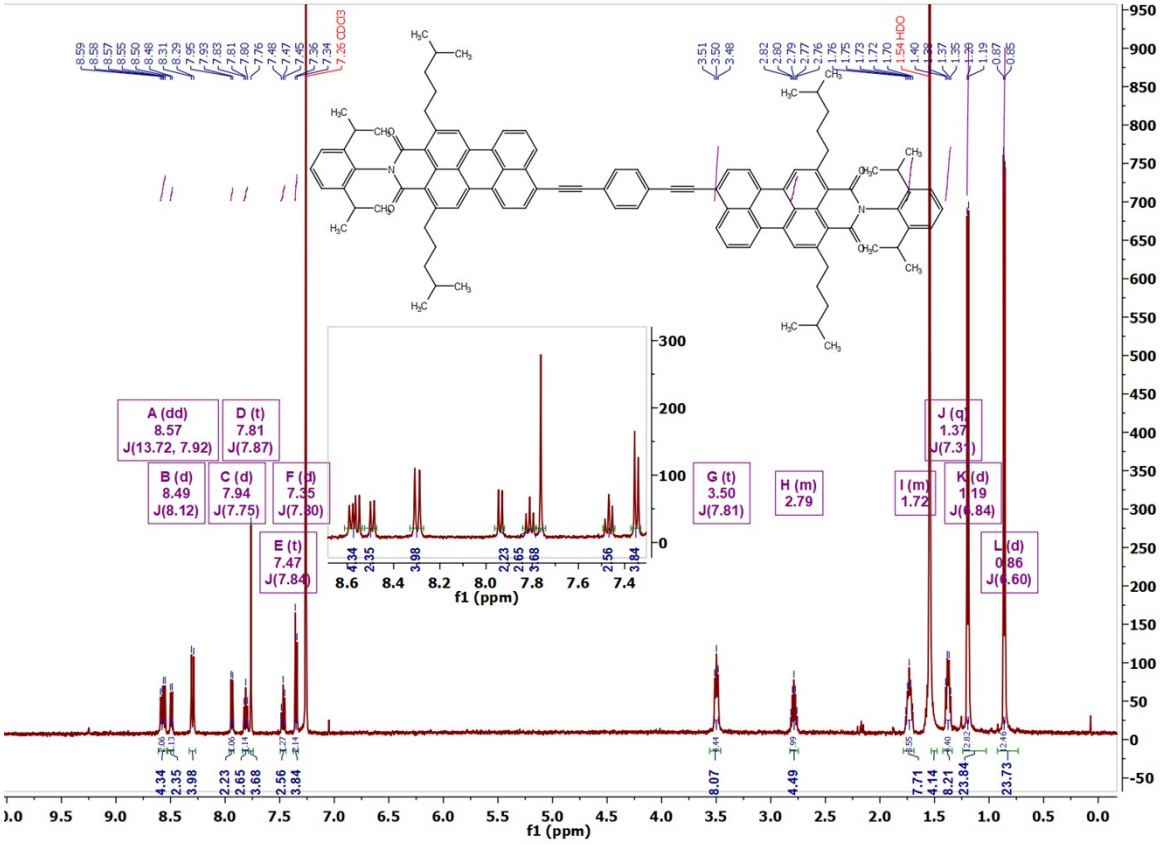


Fig. S7 ^{1}H NMR spectrum of ***p*-Ph(*o*-PMI-ac)$_2$** in $CDCl_3$ at 500 MHz.

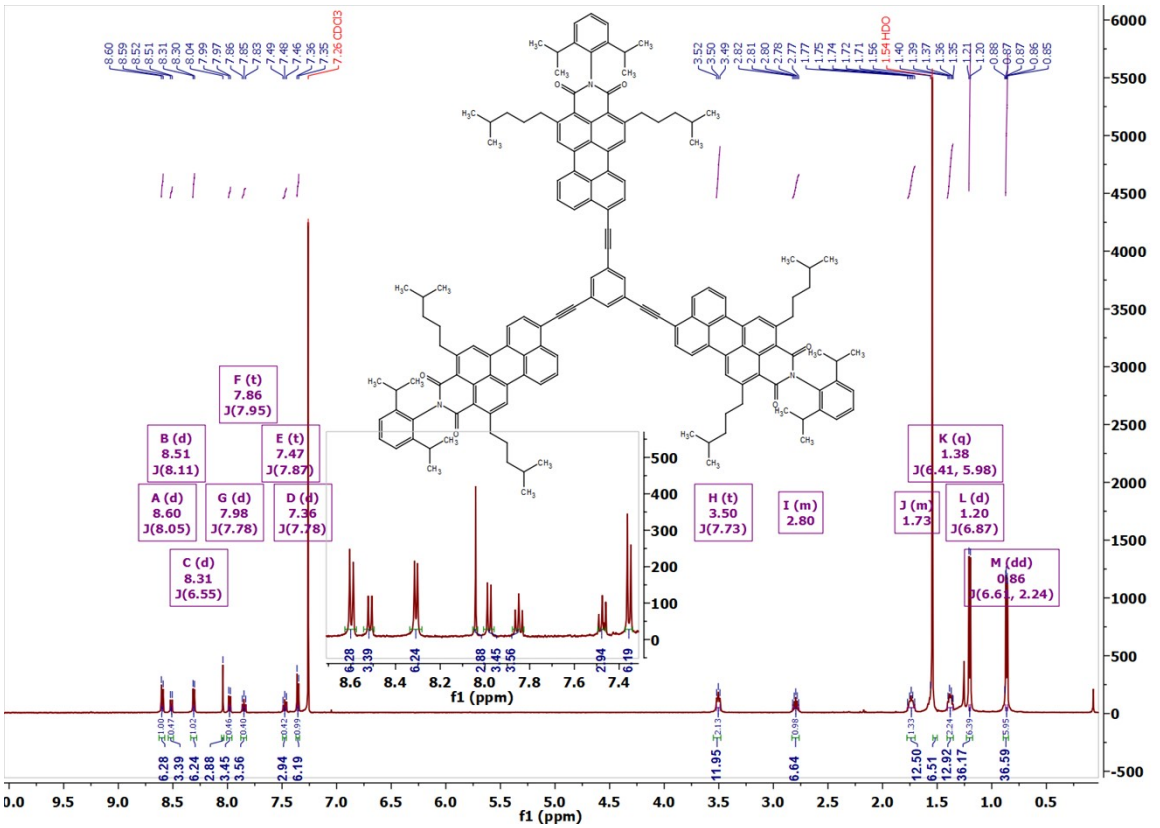


Fig. S8 ^{1}H NMR spectrum of **1,3,5-Ph(*o*-PMI-ac)$_3$** in $CDCl_3$ at 500 MHz.

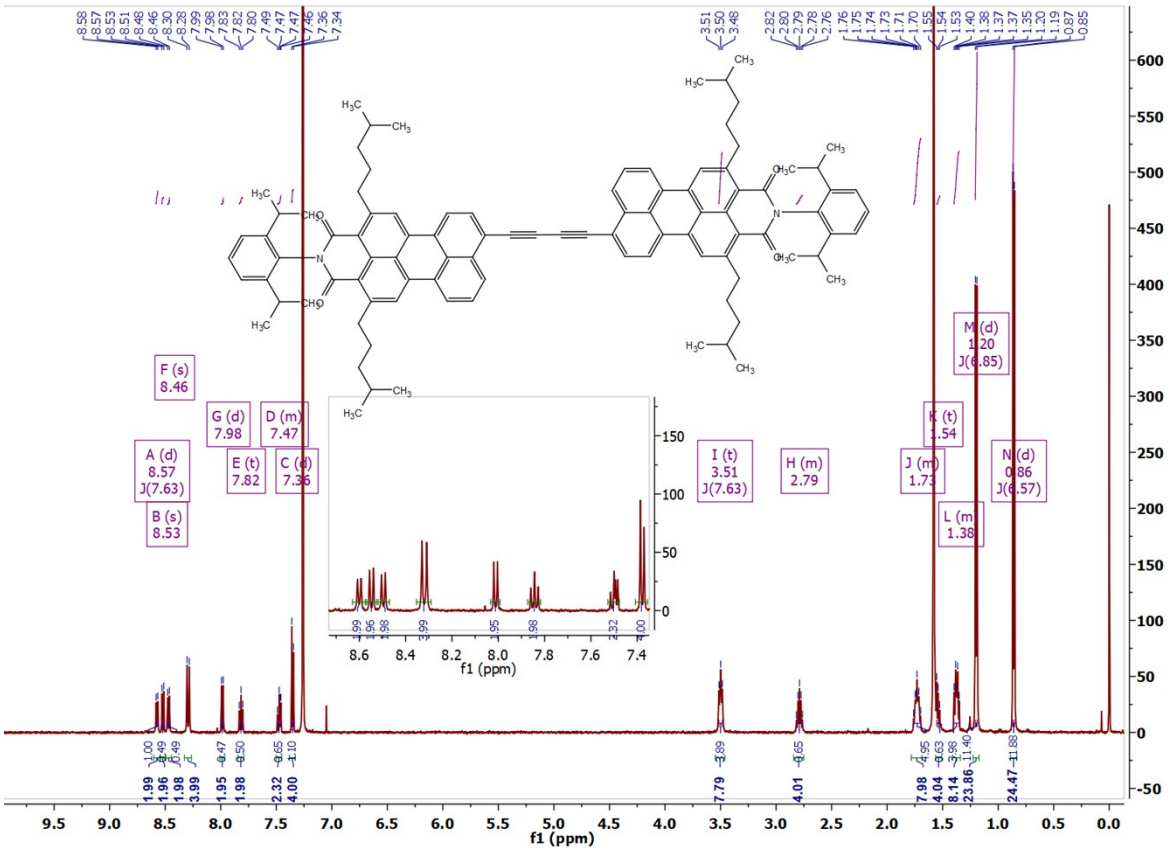


Fig. S9 ^{1}H NMR spectrum of **(*o*-PMI-ac)$_2$** in $CDCl_3$ at 500 MHz.

Note: ^{13}C NMR spectra of the dimers and trimer could not be recorded due to poor solubility of these compounds in $CDCl_3$.

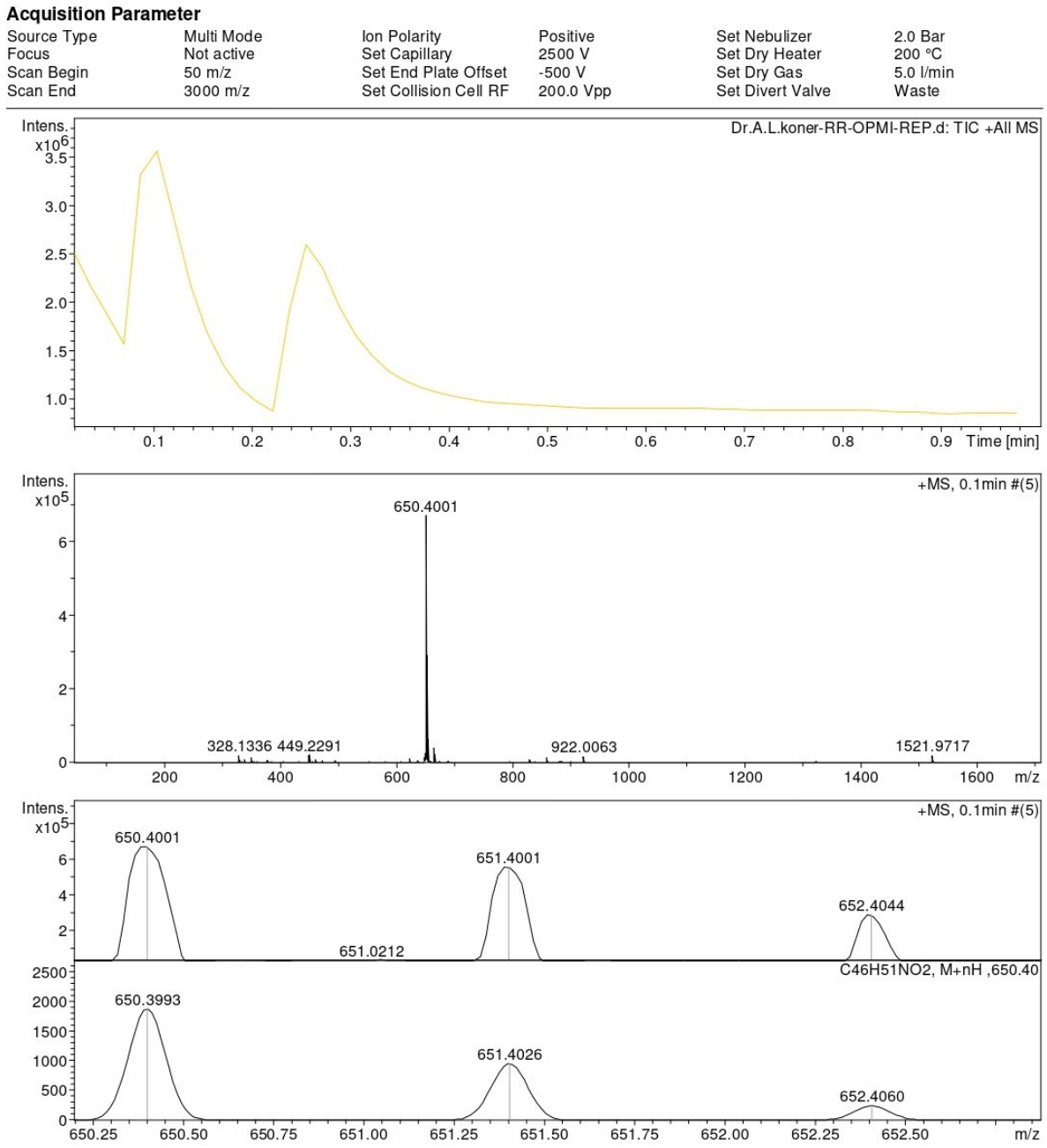


Fig. S10 APCI mass spectrum of ***o*-PMI** derivative. **Expected mass** – 649.392 and **obtained mass** – *m/z* 650.400 $[M+H]^+$.

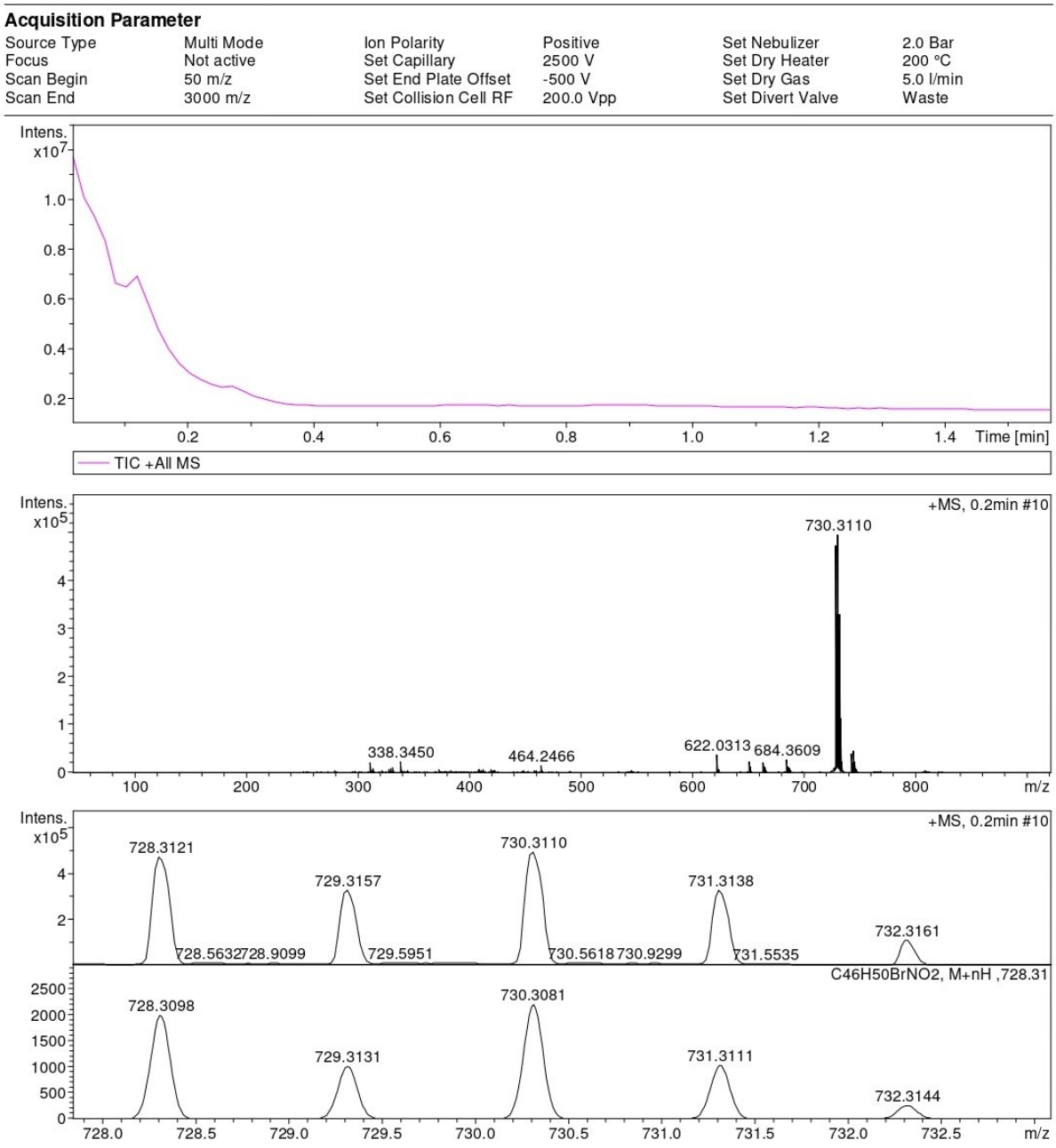


Fig. S11 APCI mass spectrum of ***o*-PMI-Br** derivative. **Expected mass** – 727.302 and **obtained mass** – *m/z* 728.312 $[M+H]^+$.

Acquisition Parameter

Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

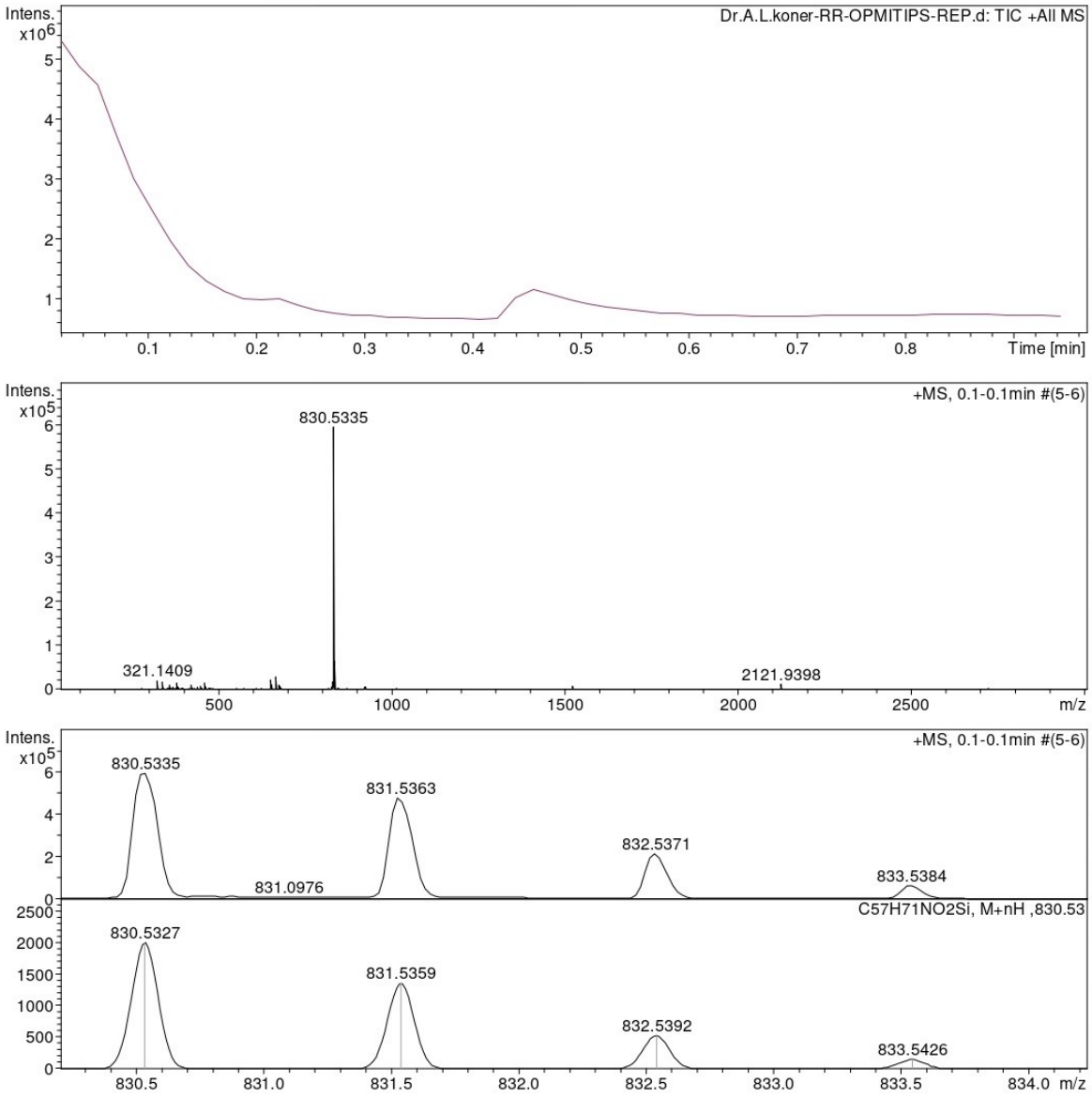


Fig. S12 APCI mass spectrum of ***o*-PMI-TIPS** derivative. **Expected mass** – 829.525 and **obtained mass** – *m/z* 830.533 $[M+H]^+$.

Acquisition Parameter

Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

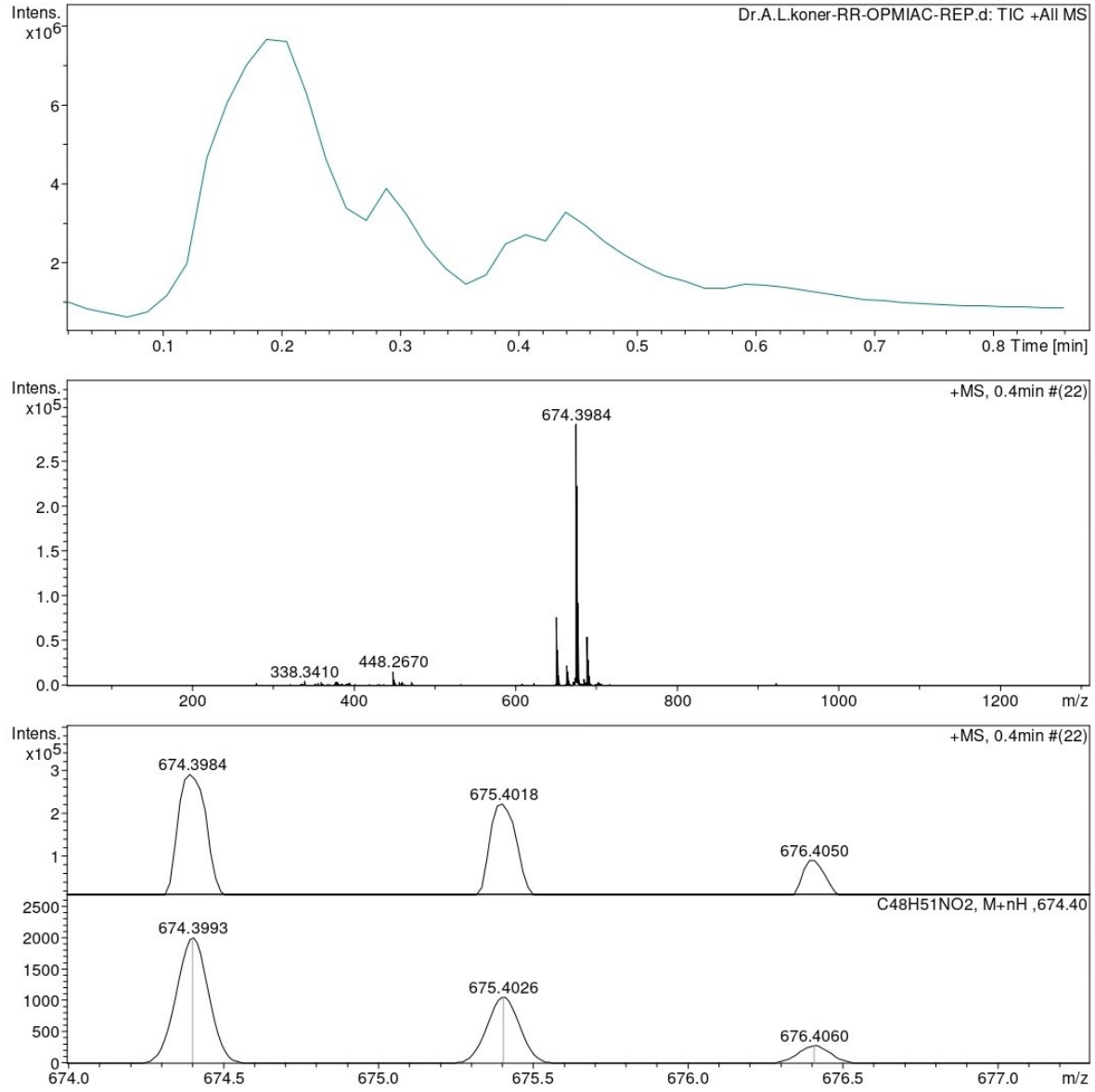


Fig. S13 APCI mass spectrum of ***o*-PMI-ac** derivative. **Expected mass** – 673.392 and **obtained mass** – *m/z* 674.398 $[M+H]^+$.

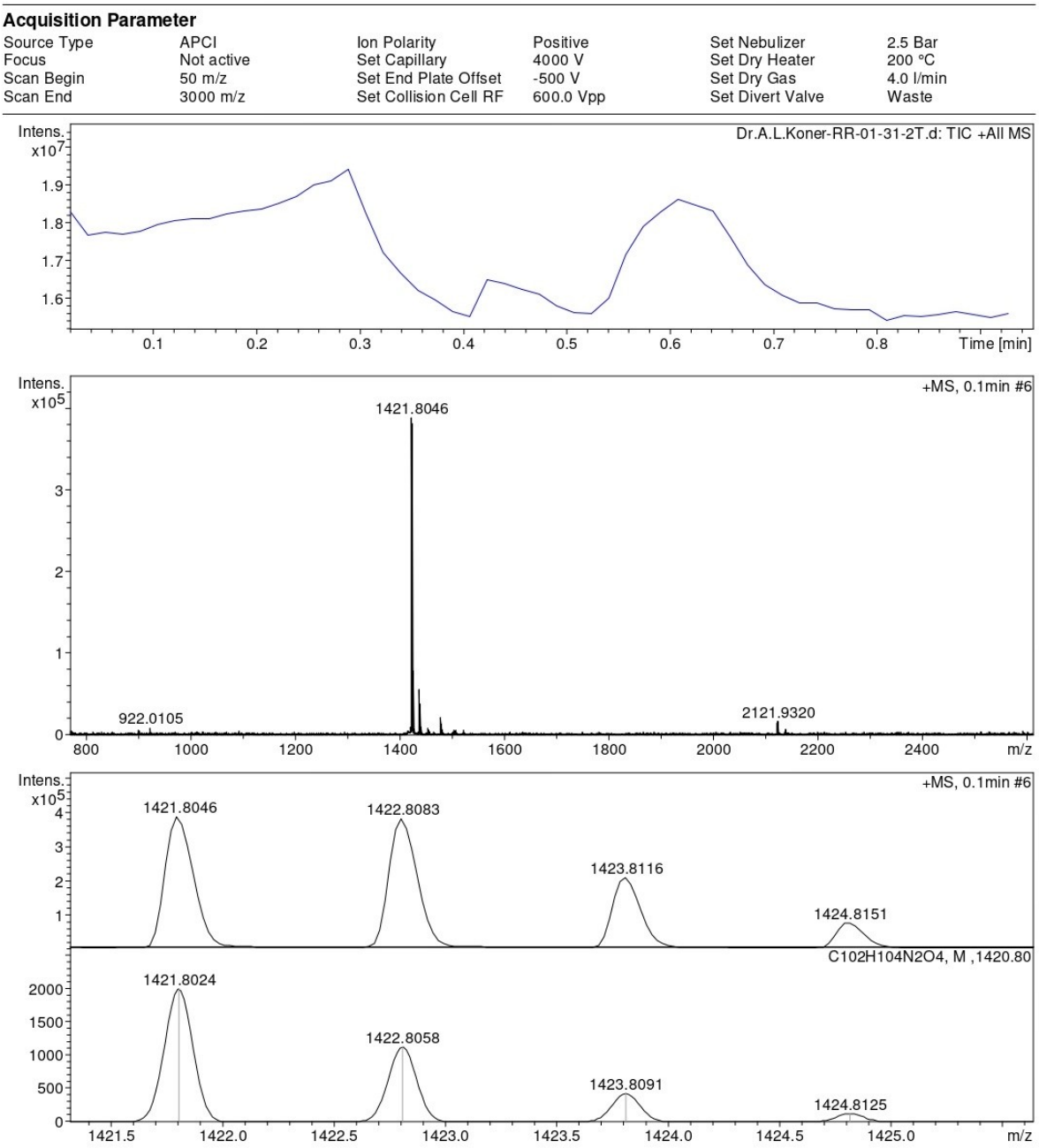


Fig. S14 APCI mass spectrum of ***o*-Ph(*o*-PMI-ac)$_2$** derivative. **Expected mass** – 1421.803 and **obtained mass** – *m/z* 1421.805 $[M]^+$.

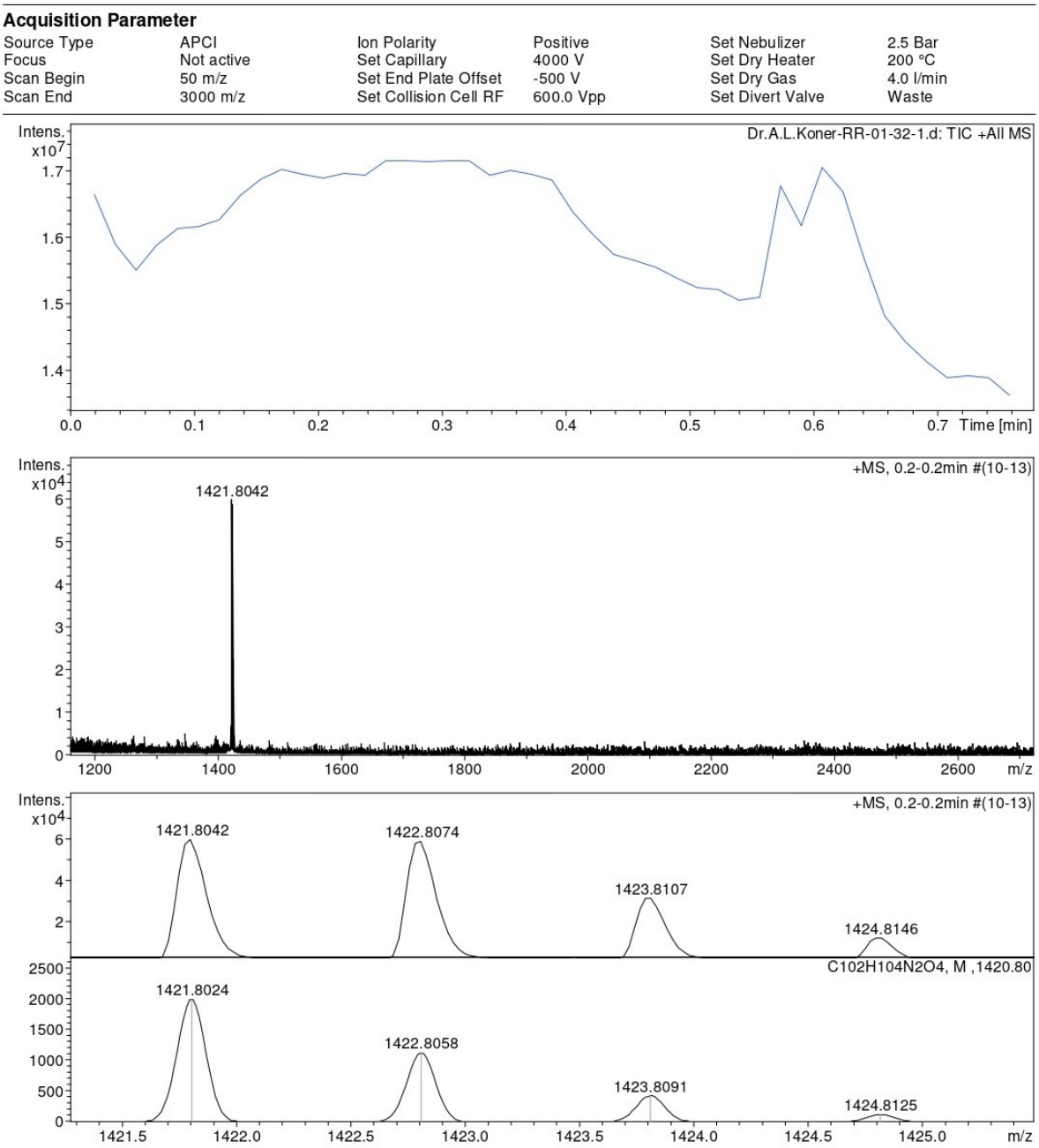


Fig. S15 APCI mass spectrum of ***m*-Ph(o-PMI-ac)$_2$** derivative. **Expected mass** – 1421.803 and **obtained mass** – *m/z* 1422.804 $[M]^+$.

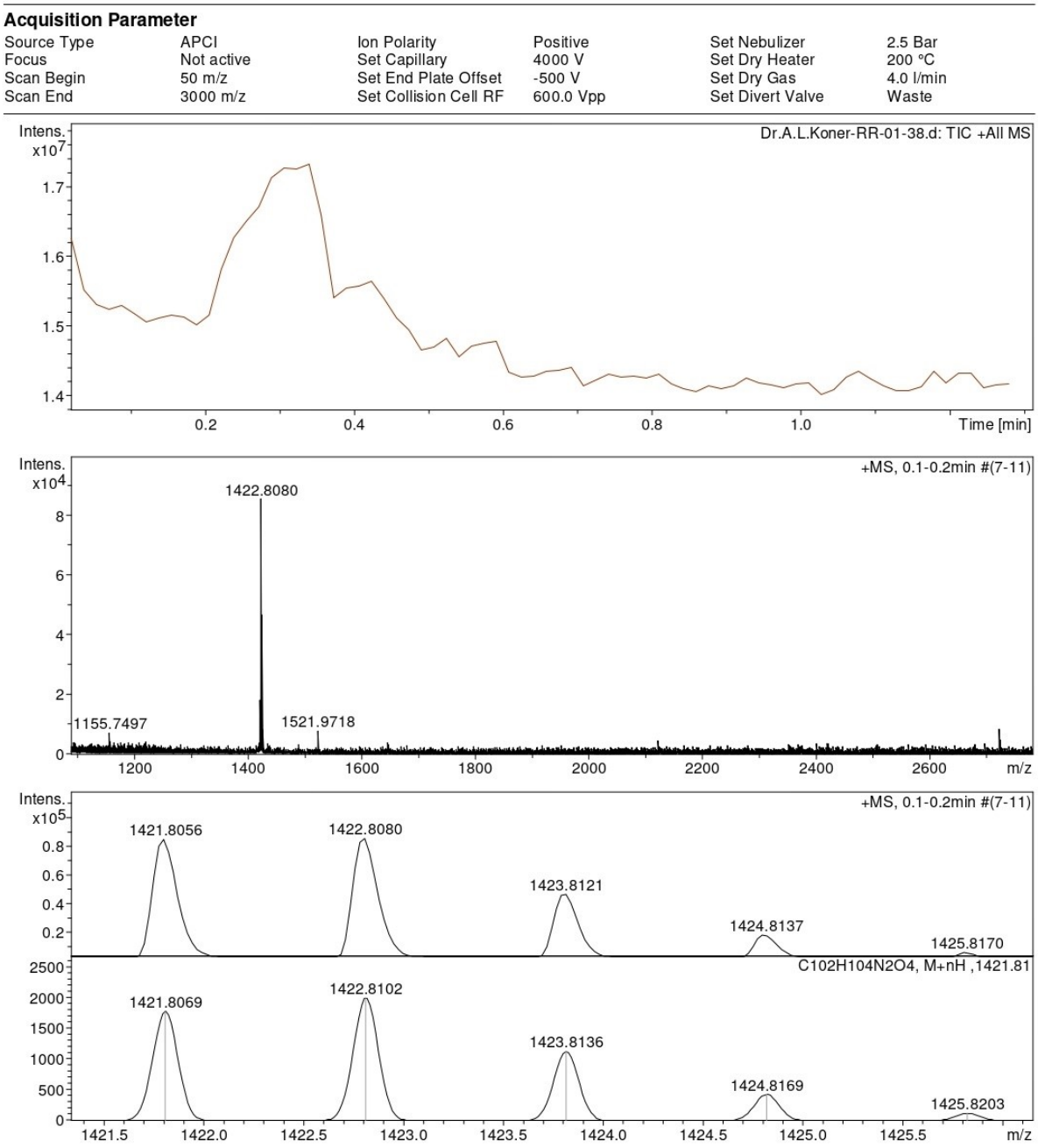


Fig. S16 APCI mass spectrum of ***p*-Ph(o-PMI-ac)$_2$** derivative. **Expected mass** – 1421.803 and **obtained mass** – *m/z* 1422.808 $[M+H]^+$.

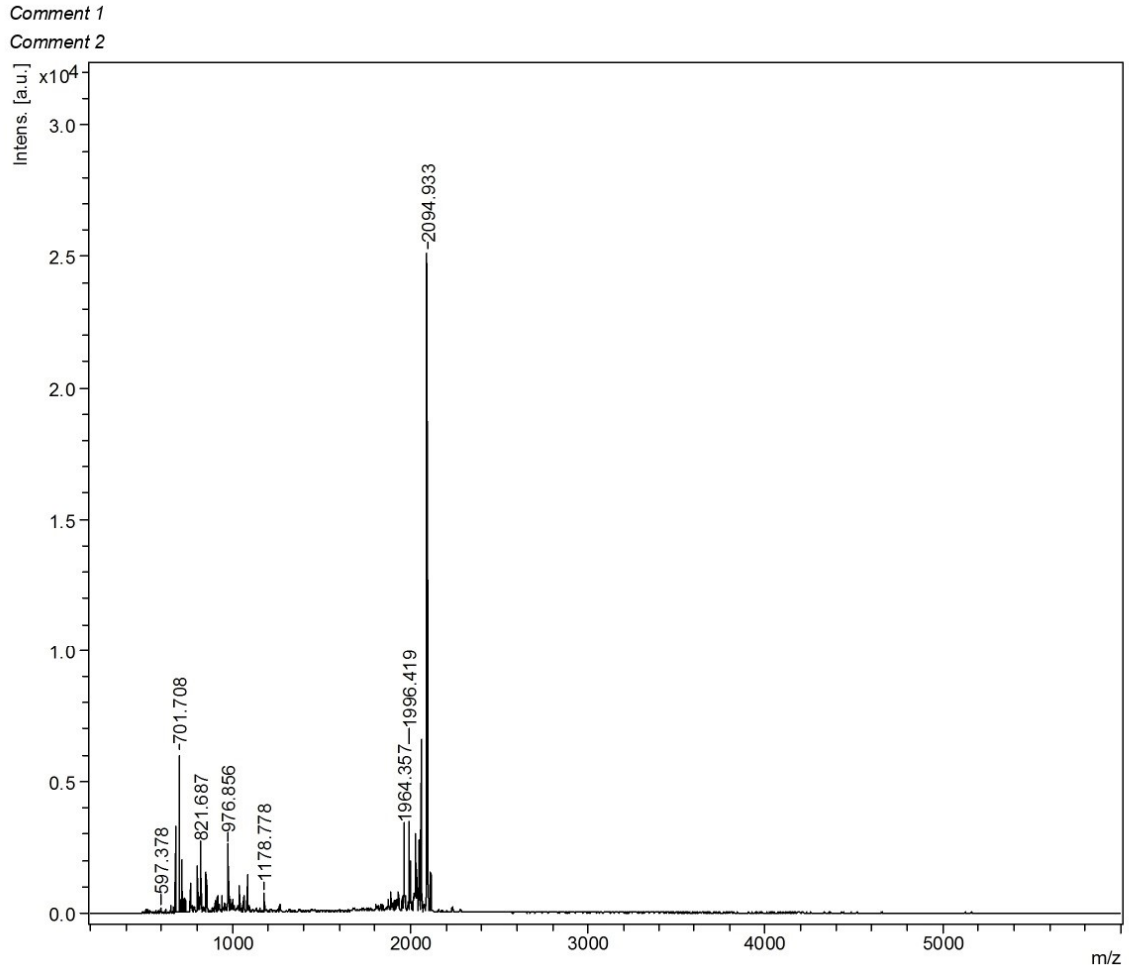


Fig. S17 MALDI mass spectrum of **1,3,5-Ph(*o*-PMI-ac)$_3$** derivative. **Expected mass** –2094.183 and **obtained mass** – *m/z* 2094.933.

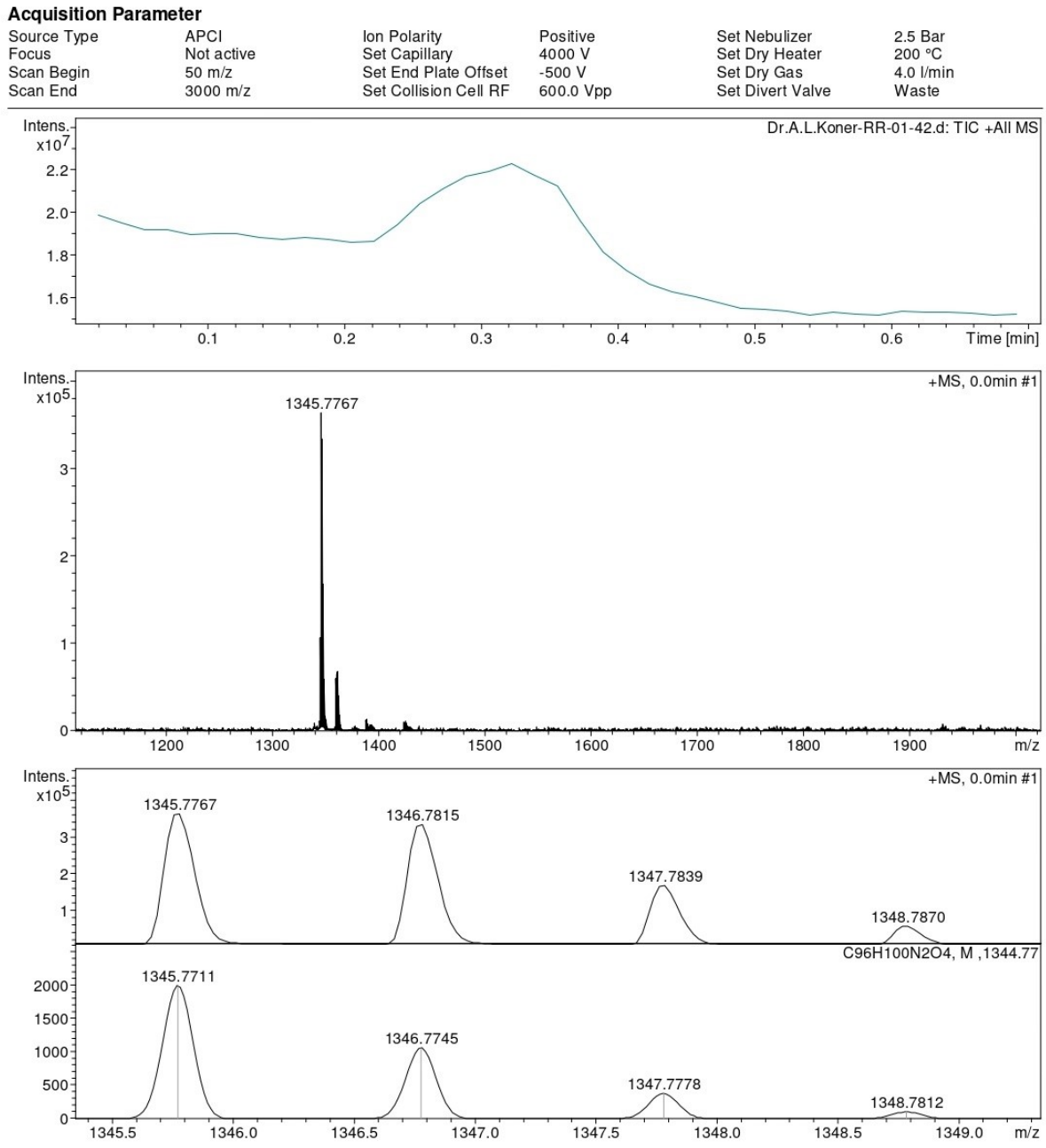


Fig. S18 APCI mass spectrum of **(*o*-PMI-ac)$_2$** derivative. **Expected mass** –1345.772 and **obtained mass** – *m/z* 1345.777 $[M]^+$.

IV. Steady-state absorption and emission studies:

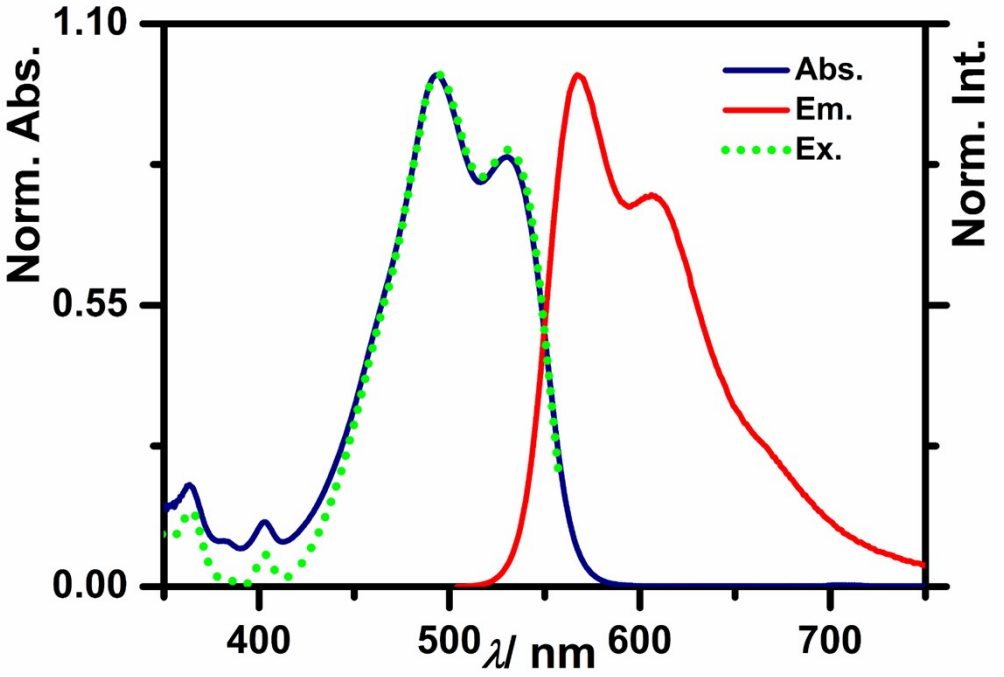


Fig. S19 Normalized absorption, emission, and excitation spectra of ***o*-Ph(o-PMI-ac)$_2$** in $CHCl_3$, superimposed absorption and excitation spectra confirms optical purity.

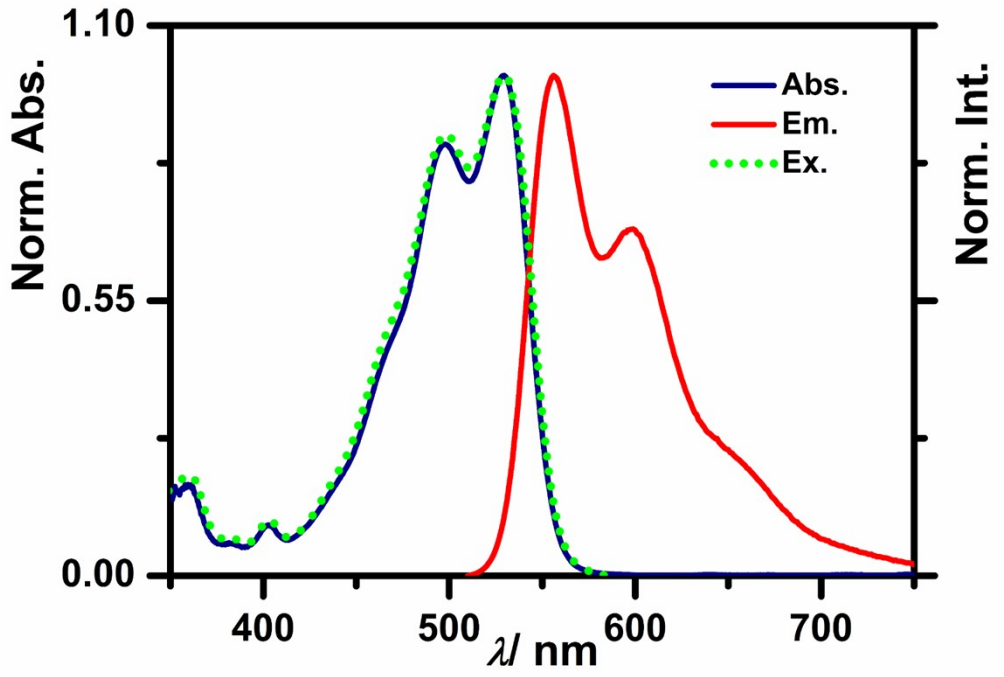


Fig. S20 Normalized absorption, emission, and excitation spectra of ***m*-Ph(o-PMI-ac)$_2$** in $CHCl_3$, superimposed absorption and excitation spectra confirms optical purity.

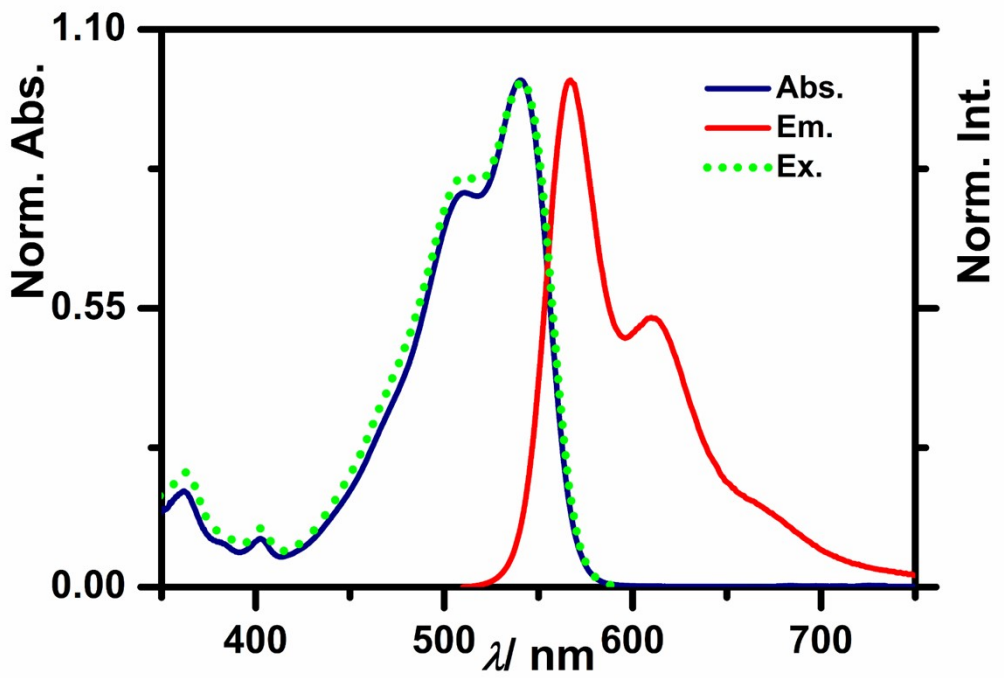


Fig. S21 Normalized absorption, emission, and excitation spectra of ***p*-Ph(o-PMI-ac)$_2$** in $CHCl_3$, superimposed absorption and excitation spectra confirms optical purity.

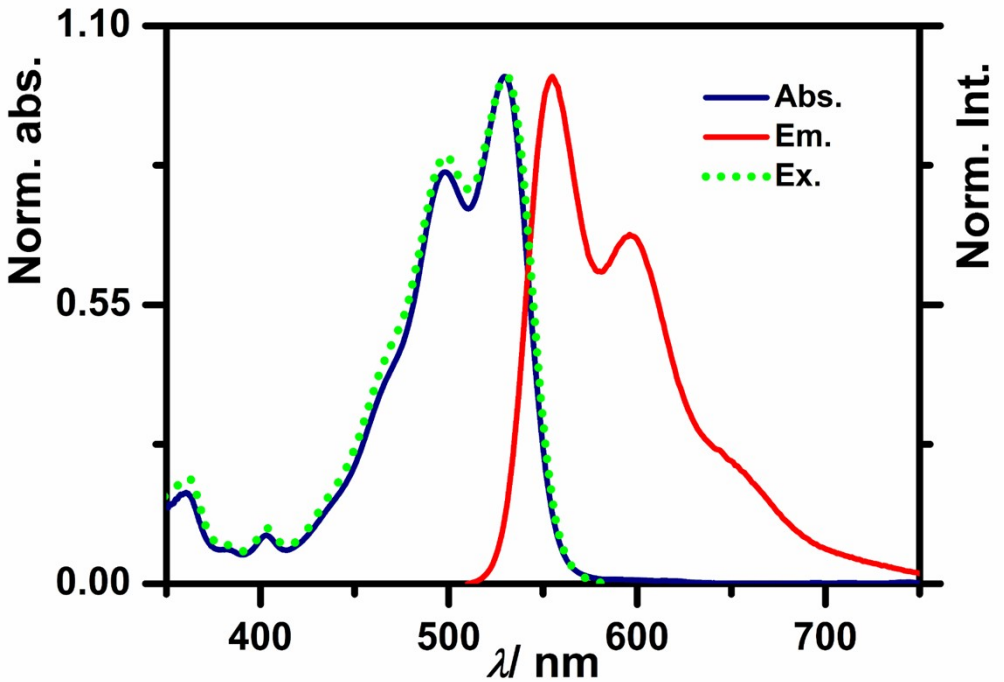


Fig. S22 Normalized absorption, emission, and excitation spectra of **1,3,5-Ph(*o*-PMI-ac)$_3$** in $CHCl_3$, superimposed absorption and excitation spectra confirms optical purity.

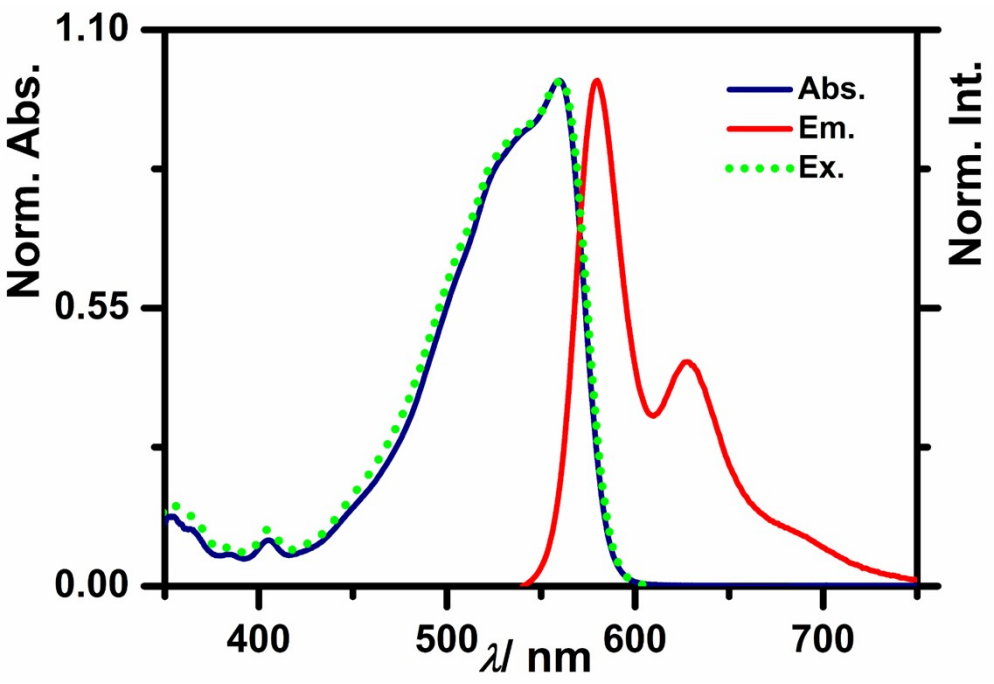


Fig. S23 Normalized absorption, emission, and excitation spectra of **(*o*-PMI-ac)$_2$** in $CHCl_3$, superimposed absorption and excitation spectra confirms optical purity.

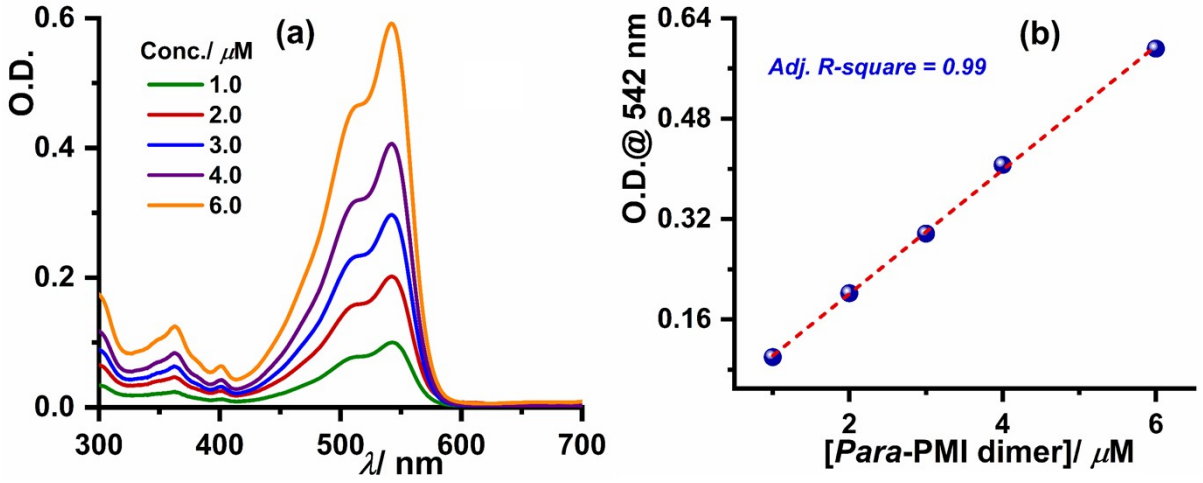


Fig. S24 (a) Concentration-dependent absorption spectra of ***p*-Ph(o-PMI-ac)$_2$** in DMF (b) plot of O.D. *vs* concentration in DMF showing a linear increment.

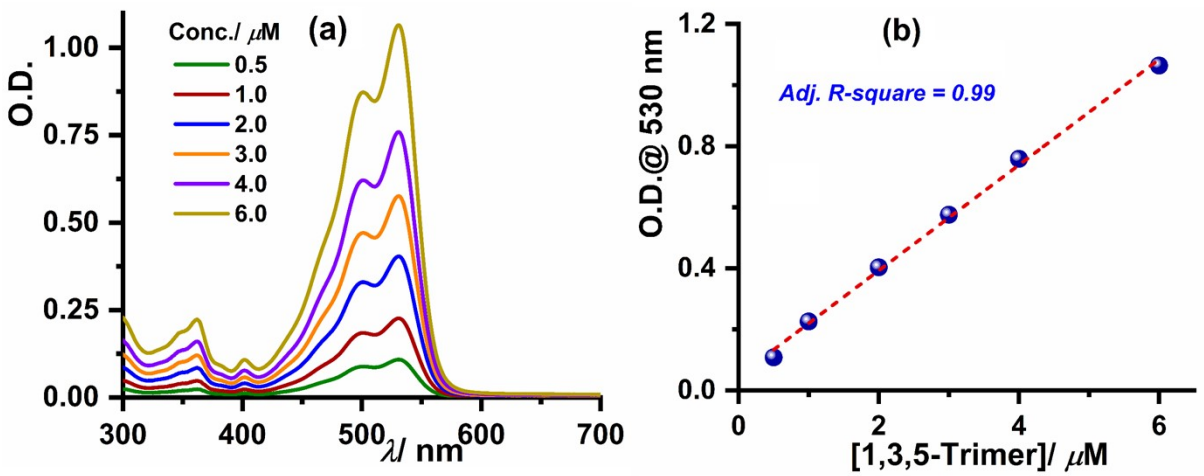


Fig. S25 (a) Concentration-dependent absorption spectra of **1,3,5-Ph(*o*-PMI-ac)$_3$** in DMF (b) plot of linear enhancement of O.D. *vs* concentration in DMF showing linear increment.

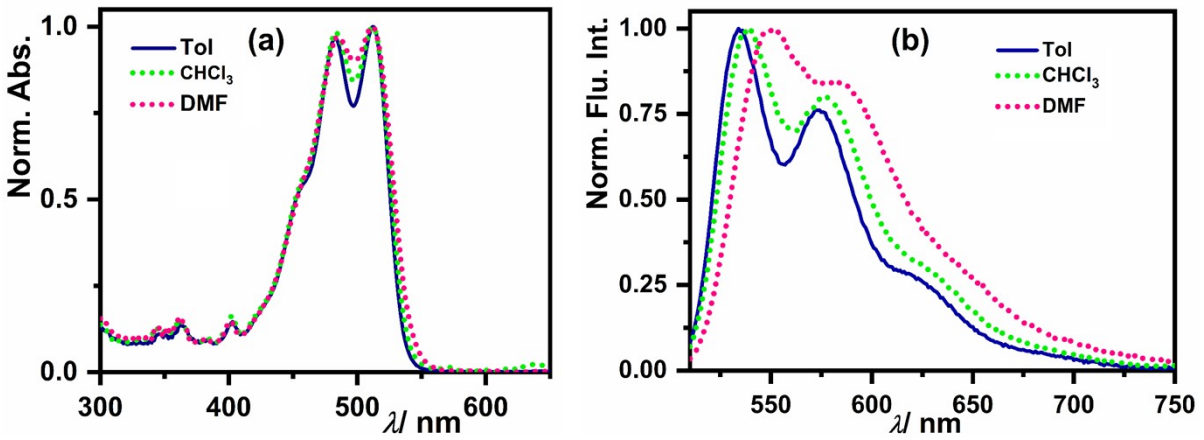


Fig. S26 Normalized (a) absorption and (b) emission spectra of ***o*-PMI-ac** monomer (c = 2.0 μM) in the given solvents.

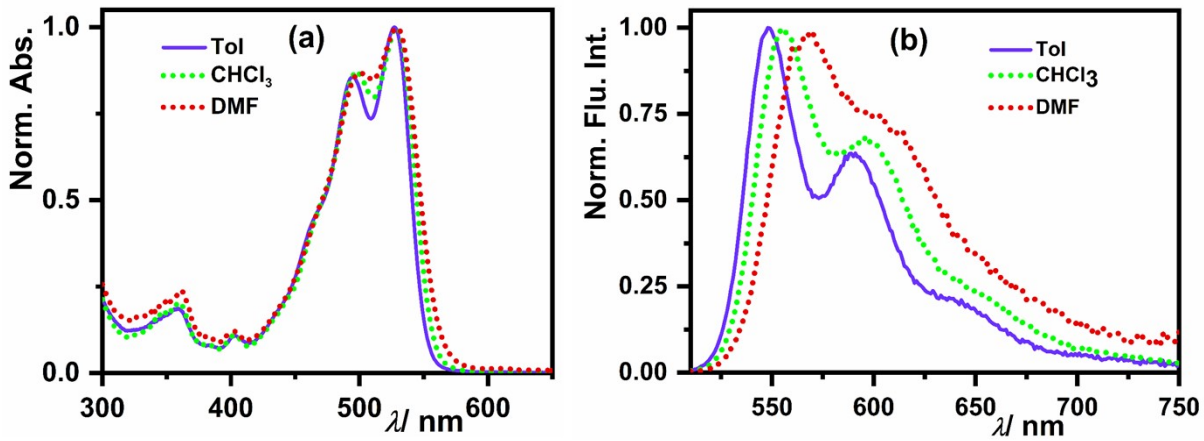


Fig. S27 Normalized (a) absorption and (b) emission spectra of ***m*-Ph(*o*-PMI-ac)$_2$** (c = 1.0 μM) in the given solvents.

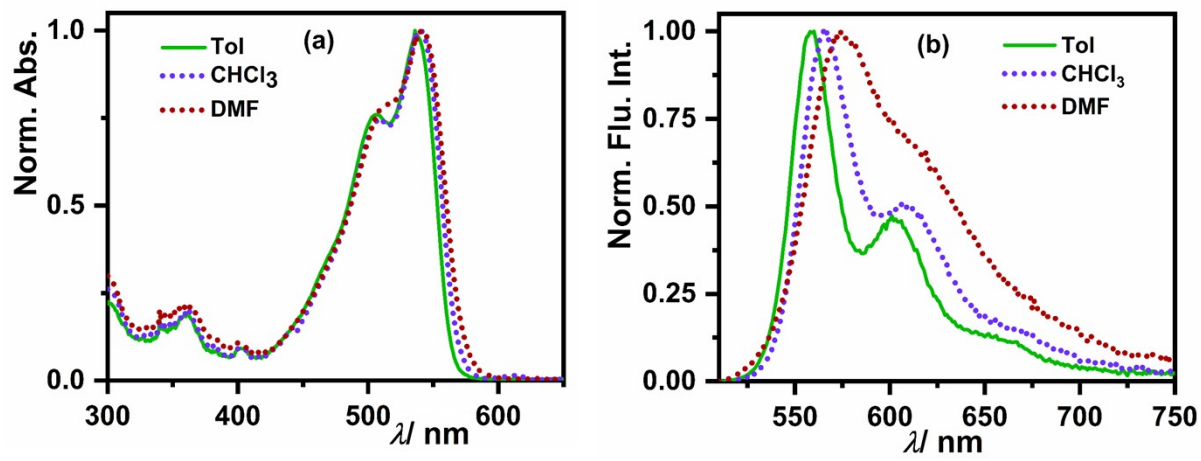


Fig. S28 Normalized (a) absorption and (b) emission spectra of ***p*-Ph(*o*-PMI-ac)$_2$** (c = 1.0 μM) in the given solvents.

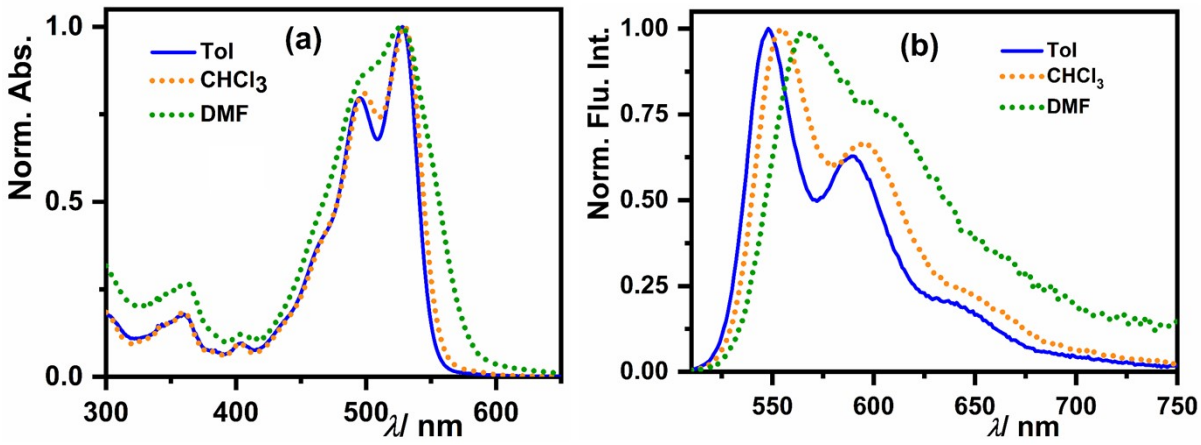


Fig. S29 Normalized (a) absorption and (b) emission spectra of **1,3,5-Ph(*o*-PMI-ac)$_3$** (c = 1.0 μM) in the given solvents.

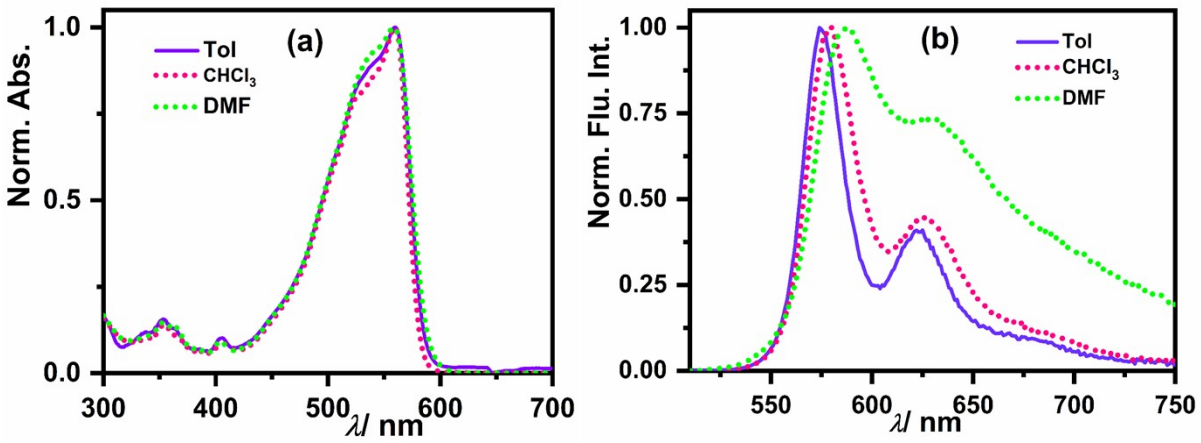


Fig. S30 Normalized (a) absorption and (b) emission spectra of self-coupled **(*o*-PMI-ac)$_2$** (c = 1.0 μM) in the given solvents.

Solvatochromism analysis:

The synthesized PMI monomer displays a positive solvatochromatic emission response correlated with solvent polarity. The solvatochromatic shifts were analyzed using the Lippert–Mataga model, employing equations 1 and 2.

$\Delta\nu$ in equation 1 represents the observed Stokes' shift of the lowest energy electronic transition (in cm^{-1}), Δf is the solvent polarizability parameter, a is the Onsager cavity radius of the dipole, μ_e and μ_g are the dipoles of the excited and ground states, and h and c denote Plank's constant and the speed of light, respectively. Δf, further is a function of ε and n represent the solvent dielectric constant and refractive index values, and given by equation 2.

$$\Delta\nu = \frac{2\Delta f}{hca^3}(\mu_e - \mu_g)^2 + C \quad (1)$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

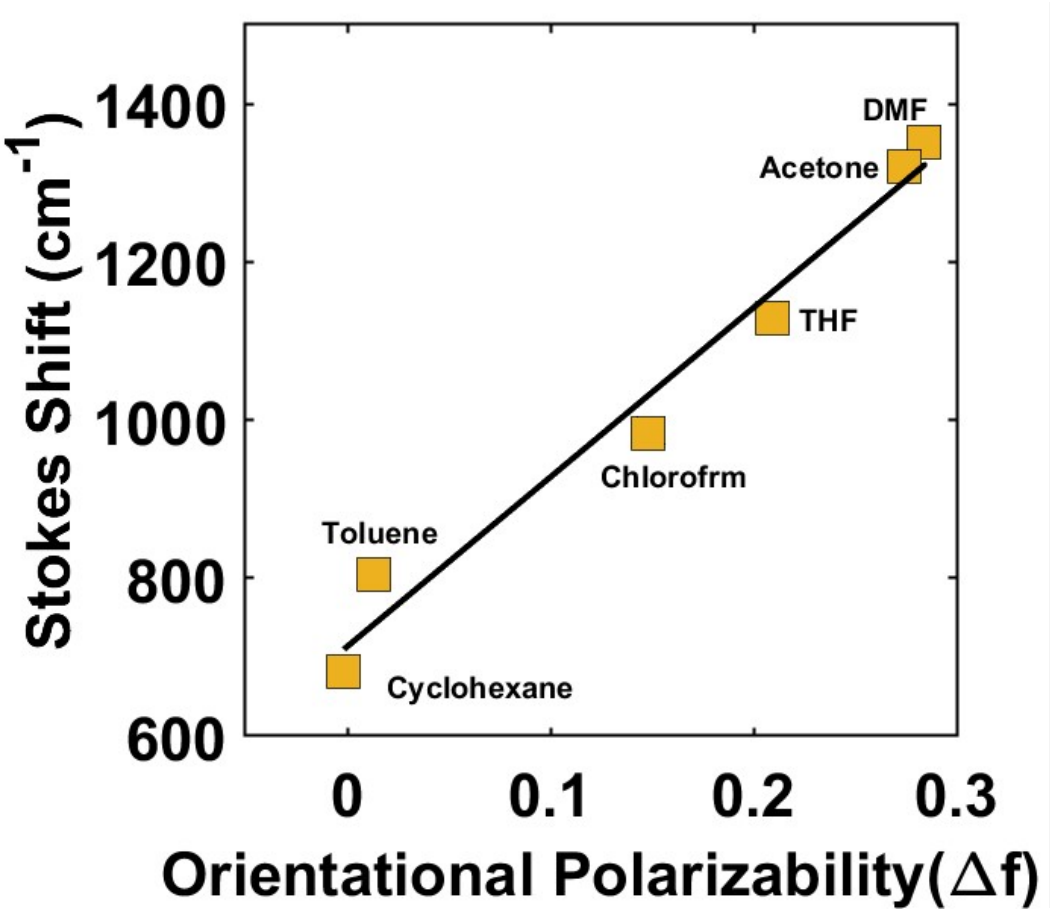


Fig. S31 Lippert–Mataga plot of the Stokes' shift in solvents of increasing polarity for ***o*-PMI-ac** monomer.

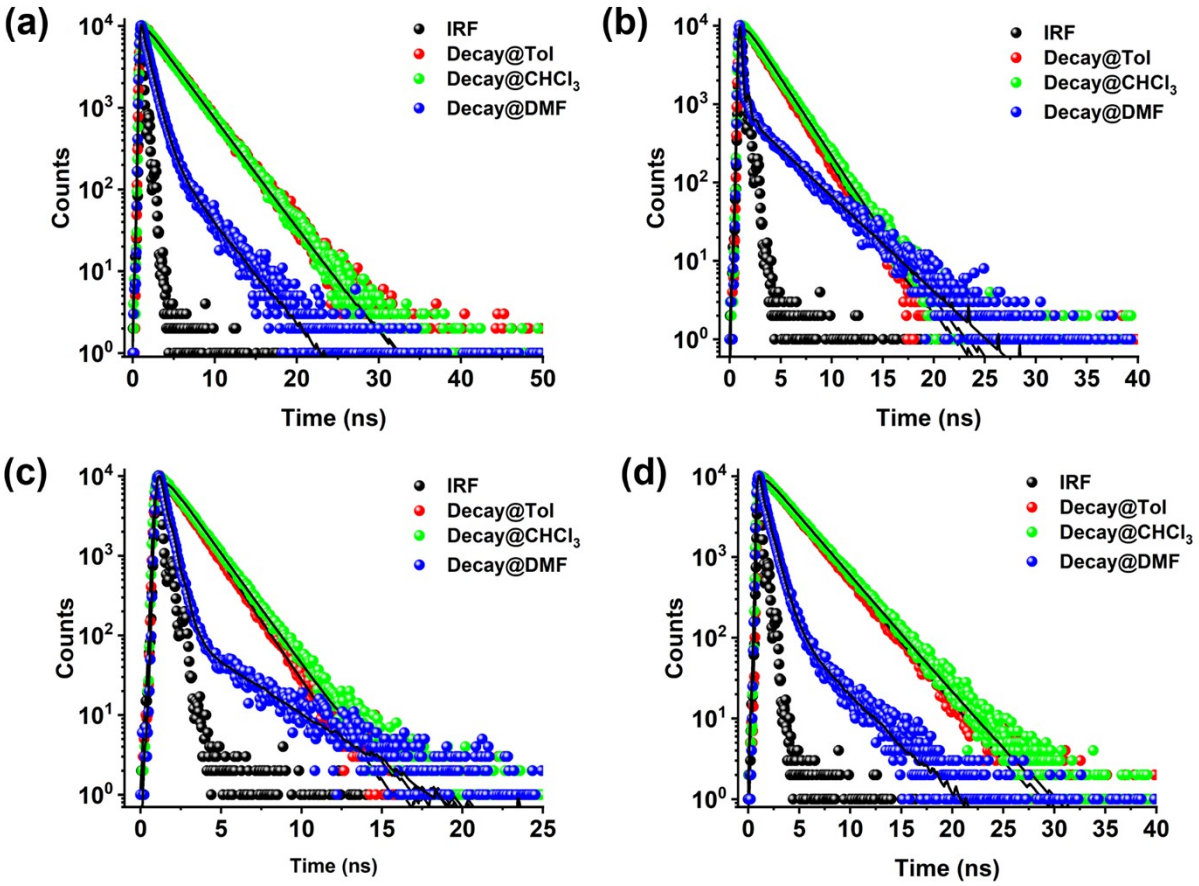


Fig. S32 Time-resolved fluorescence decay of (a) ***m*-Ph(*o*-PMI-ac)$_2$**, (b) ***p*-Ph(*o*-PMI-ac)$_2$**, (c) **(*o*-PMI-ac)$_2$**, and (d) **1,3,5-Ph(*o*-PMI-ac)$_3$** in those three solvents.

Table S1. Photophysical parameters of all synthesized PMI derivatives in solution.

Comp	Solvent	$\lambda_{max.}^{Abs.}$/ nm[a]	A_{0-0}/A_{0-1}	$\lambda_{max.}^{Em.}$/ nm[b]	Stokes shift/ nm[c]	τ_{avg}/ ns[d]	Φ_{Fl}/ %[e]
***o*-PMI-ac**	Tol	512	1.03	534	22	4.1	79 ± 1.2
	$CHCl_3$	511	1.02	538	27	4.4	71 ± 1.0
	DMF	511	1.03	548	37	4.5	54 ± 1.3
***o*-Ph(*o*-PMI-ac)$_2$**	Tol	491	0.85	557	66	4.2	75 ± 0.5
	$CHCl_3$	490	0.84	567	77	4.6	64 ± 0.5
	DMF	493	0.83	581	88	0.4	< 1.0
***m*-Ph(*o*-PMI-ac)$_2$**	Tol	527	1.16	548	21	3.2	74 ± 0.4
	$CHCl_3$	529	1.15	554	25	3.3	65 ± 0.4
	DMF	529	1.15	568	39	0.9	15 ± 1.7
***p*-Ph(*o*-PMI-ac)$_2$**	Tol	536	1.30	558	22	2.2	73 ± 0.7
	$CHCl_3$	540	1.34	566	26	2.3	64 ± 0.7
	DMF	540	1.26	574	34	3.4	12 ± 3.8
1,3,5-Ph(*o*-PMI-ac)$_3$	Tol	527	1.25	547	20	2.9	77 ± 0.4
	$CHCl_3$	528	1.24	554	26	3.1	69 ± 0.4
	DMF	527	1.15	567	40	0.7	8 ± 3.6
(*o*-PMI-ac)$_2$	Tol	560	1.16	574	14	1.5	48 ± 1.4
	$CHCl_3$	560	1.25	580	20	1.6	64 ± 2.5
	DMF	558	1.11	588	30	1.4	<1.0

[a] Absorption maxima and [b] emission maxima of all derivatives in above mentioned solvents; [c] represents Stokes shifts [$\lambda_{max}^{Em.}$ - $\lambda_{max}^{Abs.}$]; [d] average fluorescence lifetime values and [e] absolute fluorescence QY in solution was measured by following integrating sphere method.

Table S2. Time-resolved decay parameters for all PMI derivatives in three solvents.

Compound	Entry	τ_1 (cont%)	τ_2 (cont%)	τ_{avg}/ ns
***o*-PMI-ac**	Tol	4.1	-	4.1
	$CHCl_3$	4.4	-	4.4
	DMF	4.5	-	4.5
***o*-Ph(*o*-PMI-ac)$_2$**	Tol	4.2	-	4.2
	$CHCl_3$	4.6	-	4.6
	DMF	0.3 (90%)	1.7 (10%)	0.4
***m*-Ph(*o*-PMI-ac)$_2$**	Tol	3.2 (100%)	-	3.2
	$CHCl_3$	3.3 (100%)	-	3.3
	DMF	0.4 (15%)	0.9 (85%)	0.9
***p*-Ph(*o*-PMI-ac)$_2$**	Tol	2.2 (100%)	-	2.2
	$CHCl_3$	2.3 (100%)	-	2.3
	DMF	0.1 (72%)	3.6 (28%)	3.4
1,3,5-Ph(*o*-PMI-ac)$_3$	Tol	2.9 (100%)	-	2.9
	$CHCl_3$	3.1 (100%)	-	3.1
	DMF	0.3 (31%)	0.8 (69%)	0.7
(*o*-PMI-ac)$_2$	Tol	1.5 (100%)	-	1.5
	$CHCl_3$	1.6 (100%)	-	1.6
	DMF	0.3 (95%)	3.4 (5%)	1.4

Here, τ_{avg} is calculated using the following equation:

$$\tau_{avg} = \sum a_i \tau_i^2 \Big/ \sum a_i \tau_i$$

V. Theoretical calculations:

Table S3. Calculated absorption wavelengths (λ, nm) and transition electric dipole moments (|TEDM|, au) at CAM-B3LYP/def2-TZVP level of theory. The oscillator strengths are given in parentheses.

		$\lambda_{abs}^{calc}(f)$	**|TEDM|**
PMI-monomer	Gas-Phase	428 (1.09)	3.42
	Toluene	455 (1.28)	3.82
	Chloroform	453 (1.28)	3.81
	DMF	453 (1.28)	3.81
ortho-PMI dimer	Gas-Phase	430 (1.10)	4.99
	Toluene	460 (2.11)	5.62
	Chloroform	458 (2.11)	5.61
	DMF	458 (2.11)	5.61
meta-PMI dimer	Gas-Phase	461 (2.46)	6.10
	Toluene	481 (2.57)	6.38
	Chloroform	480 (2.58)	6.38
	DMF	481 (2.59)	6.40
para-PMI dimer	Gas-Phase	482 (3.74)	7.70
	Toluene	501 (3.84)	7.96
	Chloroform	500 (3.85)	7.96
	DMF	500 (3.86)	7.97

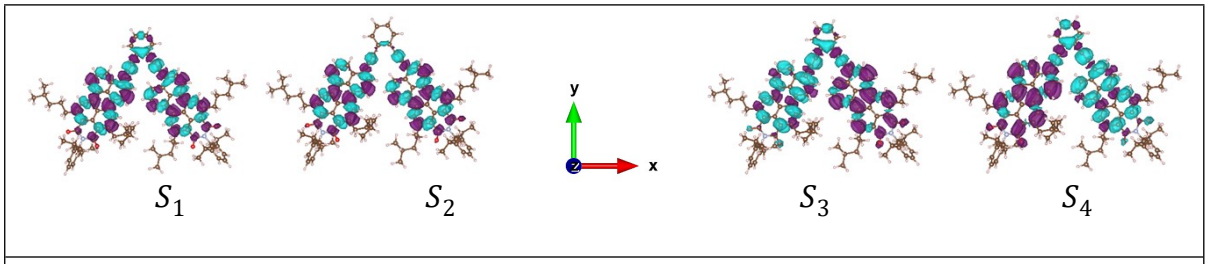
Table S4. Calculated singlet excited state energies (*E* in eV) and transition electric dipole moments (TEDM, au) at CAM-B3LYP/def2-TZVP/CPCM(Chloroform) level of theory. The oscillator strengths and polarization axis are given in the parentheses. H stands for HOMO while L stands for LUMO.

	States	E_{TZVP} (*f*)	TEDM	Major Transitions (%)	E_{SVP}(*f*)
o-PMI-ac monomer	S_1	2.74 (1.28)	3.80 (x)	H → L (96)	2.80 (1.32)
	S_2	3.75 (0.08)	– 0.74 (y)	H – 3 → L (75), H → L+3 (10)	3.81 (0.08)
	S_3	4.01 (0.01)	– 0.26 (x)	H → L+1 (27), H – 6 → L (22), H – 4 → L (16)	4.10 (0.03)
	S_4	4.05 (0.13)	– 1.02 (y)	H – 4 → L (48), H → L+3 (17)	4.10 (0.10
ortho-PMI dimer	S_1	2.53 (1.16)	– 4.30 (x)	H → L (66), H – 1 → L+1 (29)	2.58 (1.19)
	S_2	2.70 (2.11)	5.61 (y)	H – 1 → L (47), H → L+1 (48)	2.77 (2.19)
	S_3	3.38 (0.00)	– 0.19 (x)	H – 1 → L (20), H – 1 → L+1 (26), H → L+1 (24)	3.44 (0.01)
	S_4	3.42 (0.01)	– 0.32 (x)	H – 1 → L (24), H – 1 → L+1 (28), H → L+1 (22)	3.46 (0.01
meta-PMI dimer	S_1	2.58 (2.58)	6.38 (x)	H – 1 → L (47), H → L+1 (45)	2.64 (2.65)
	S_2	2.68 (0.82)	– 4.48 (y)	H – 1 → L (45), H → L+1 (50)	2.74 (0.86)
	S_3	3.68 (0.01)	– 0.35 (x)	H – 2 → L+1 (18), H – 2 → L (27), H → L+1 (23)	3.73 (0.01)
	S_4	3.70 (0.17)	1.35 (y)	H – 2 → L+1 (23), H – 2 → L (14), H → L (22)	3.75 (0.14)
para-PMI dimer	S_1	2.48 (3.84)	– 7.96 (x)	H → L (68), H – 1 → L+1 (26)	2.53 (3.94)
	S_2	2.68 (0.01)	0.38 (y)	H – 1 → L (45), H → L+1 (48)	2.74 (0.01)
	S_3	3.44 (0.11)	1.11 (x)	H – 2 → L (32), H – 1 → L+1 (29), H → L+2 (19)	3.50 (0.08)
	S_4	3.61 (0.02)	0.49 (y)	H – 2 → L+1 (15), H – 1 → L (33), H → L+1 (35)	3.65 (0.02)

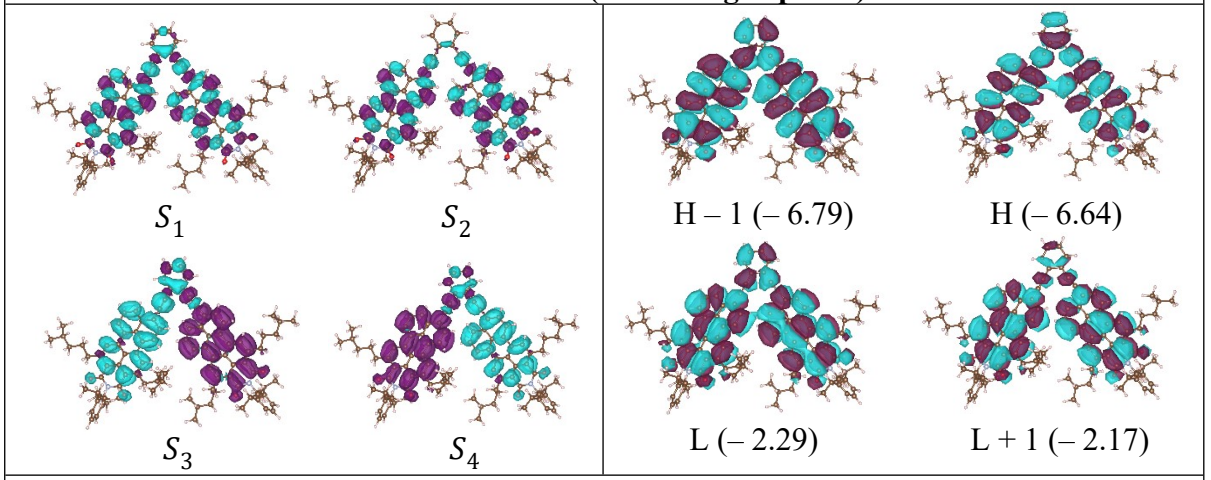
Table S5: Calculated emission wavelengths (λ, nm) at CAM-B3LYP/def2-SVP level of theory in gas-phase. The oscillator strengths are given in parentheses. The transition electric dipole moments (TEDM) are also listed. The blue-colored values are referred the absorption and emission wavelengths of *ortho*-dimer.

	λ_{abs}^{calc}	|TEDM| (au)	λ_{em}^{calc}		|TEDM| (au)	Stokes shift (nm)
PMI-monomer	417 (1.15)	3.46	Gas	452 (1.17)	3.65	35
			$CHCl_3$	484 (1.34)	4.62	

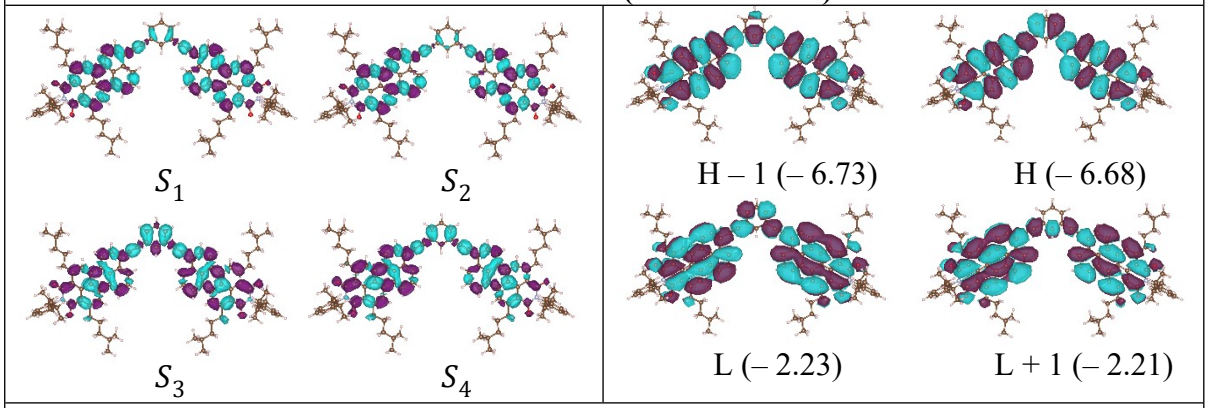
			DMF	545 (1.47)	5.13	
ortho-PMI dimer	S_1: 463 (1.14) S_2: **419 (1.89)**	4.15 5.08	**494 (1.27)** 430 (1.83)		4.41 5.07	75
meta-PMI dimer	450 (2.56)	6.15	476 (2.19)		5.60	26
para-PMI dimer	472 (3.86)	7.74	499 (4.02)		8.13	27



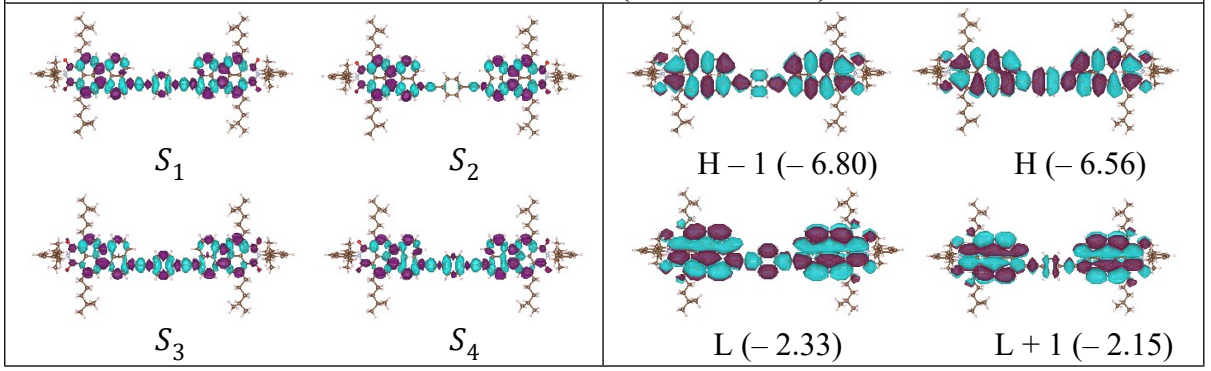
***ortho*-PMI Dimer (NTOs in gas-phase)**



***ortho*-PMI Dimer (in chloroform)**



***meta*-PMI Dimer (in chloroform)**



para-PMI Dimer (in chloroform)

Fig. S33 (Left) The NTO plots (isovalues ±0.0002 au) corresponding to the chloroform solvated singlet excited states. (Right) The frontier MOs (isovalues ±0.005 au) of *ortho*-, *meta*- and *para*-PMI dimers with their site energies (eV) in parentheses.

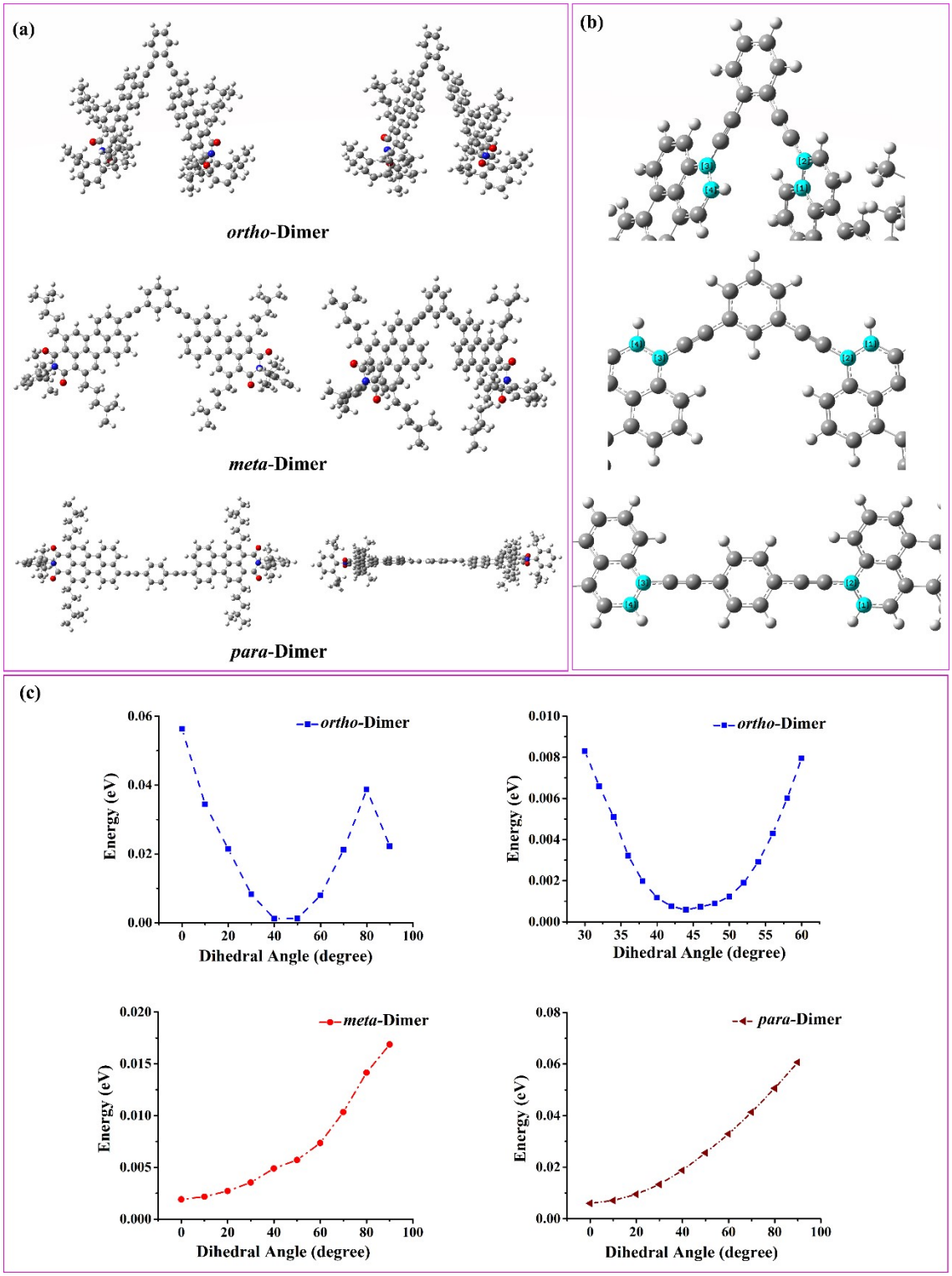


Fig. S34 (a) Optimized structures of the *ortho*-, *meta*- and *para*-PMI dimers. (b) The cyan blue-colored atoms are considered to define the dihedral angle in relax scanning. (c) Plots of calculated molecular energy versus PMI-PMI dihedral angles of the dimers.

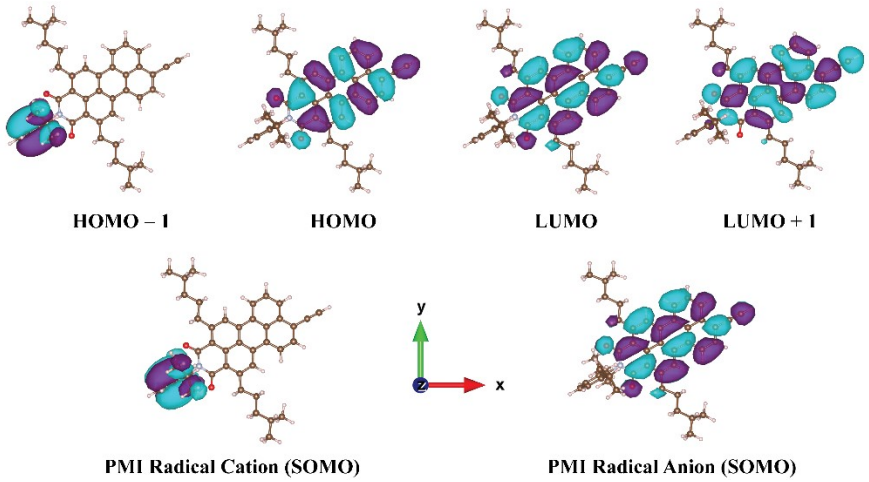


Fig. S35 Frontier MO plots of neutral PMI and singly occupied MOs (SOMOs) of the PMI radical cation and anion. The isovalues are used of ±0.01 au.

Table S6: The calculated orbital overlap values (cm^{-1}) for different dimeric structures. Blue: Maximum coupling strength, Red: Minimum coupling strength.

	φ	J_{HH}	J_{LL}	J_{HL}	$J_{H-1,H}$	$J_{L,L+1}$	$J_{H-1,L+1}$	$J_{H-1,L}$
ortho-PMI dimer	0	406.3	-240.4	-29.4	1058.6	-210.7	-438.5	-405.4
	10	-325.9	-210.2	2.9	-2079.5	-190.6	872.8	798.7
	20	-1514.8	-229.2	475.2	-4922.9	-226.4	2022.3	1861.6
	30	-798.9	-136.9	217.2	-905.4	-150.5	1194.2	1047.5
	40	577.8	-32.8	34.8	-2190.3	-96.4	1059.2	1000.7
	50	302.6	-66.7	249.0	286.0	-125.3	181.6	149.0
	60	292.6	-55.9	251.2	196.0	-94.0	148.5	124.4
	70	322.7	-45.4	207.4	184.3	-44.8	141.8	114.9
	80	-413.3	-17.3	133.1	-137.7	12.6	155.5	117.3
	90	789.2	240.4	-79.7	99.3	-147.8	259.4	207.8
meta-PMI dimer	0	-798.5	-29.3	75.8	-	-	-	-
	10	-799.3	-28.2	75.7	-	-	-	-
	20	-798.0	-28.2	75.8	-	-	-	-
	30	-798.0	-28.1	75.7	-	-	-	-
	40	-798.1	-27.9	75.2	-	-	-	-
	50	-797.4	-26.4	74.0	-	-	-	-
	60	-798.0	-26.3	74.4	-	-	-	-
	70	-795.7	-25.2	74.7	-	-	-	-
	80	-813.8	-24.3	76.7	-	-	-	-
	90	-796.1	-23.1	72.2	-	-	-	-
para-PMI dimer	0	686.1	17.3	-119.4	-	-	-	-
	10	686.9	17.3	-59.5	-	-	-	-
	20	687.8	16.3	-59.6	-	-	-	-

	30	690.6	16.4	-60.0	-	-	-	-
	40	633.0	-19.3	-63.0	-	-	-	-
	50	-645.8	-15.5	51.9	-	-	-	-
	60	643.9	-16.4	51.5	-	-	-	-
	70	643.3	-16.2	51.1	-	-	-	-
	80	641.3	-15.9	50.6				
	90	638.7	-15.6	50.0				

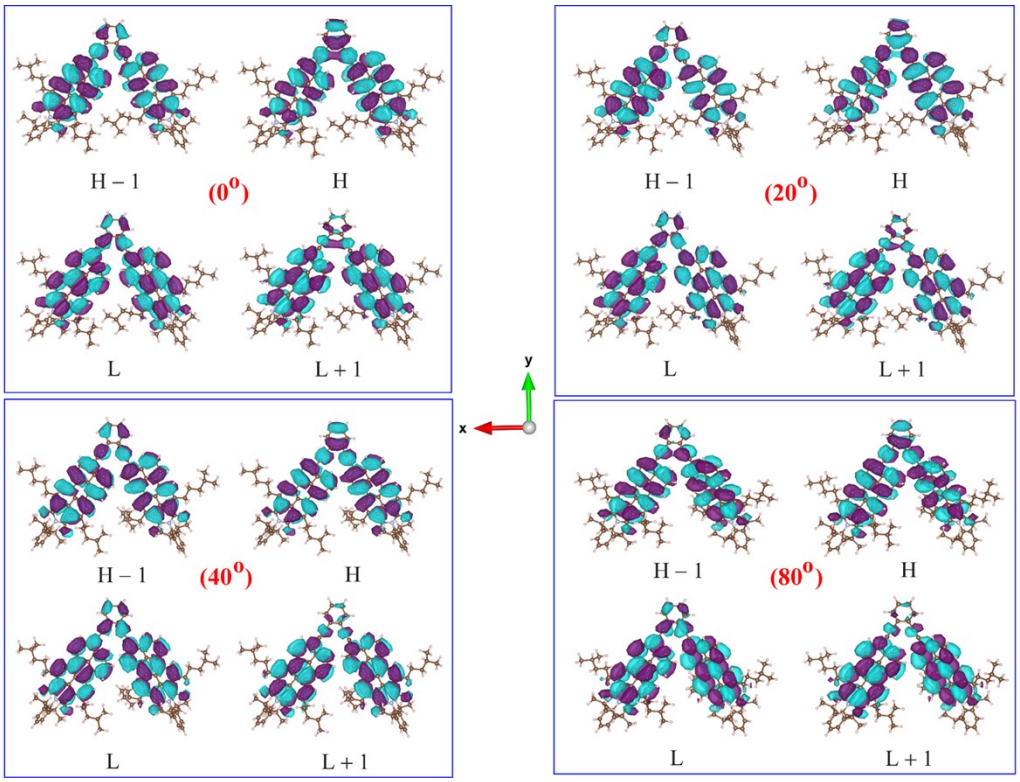


Fig. S36 The frontier MOs (isovalues ±0.01 au) of *ortho*-PMI dimers with different PMI-PMI dihedral angles.

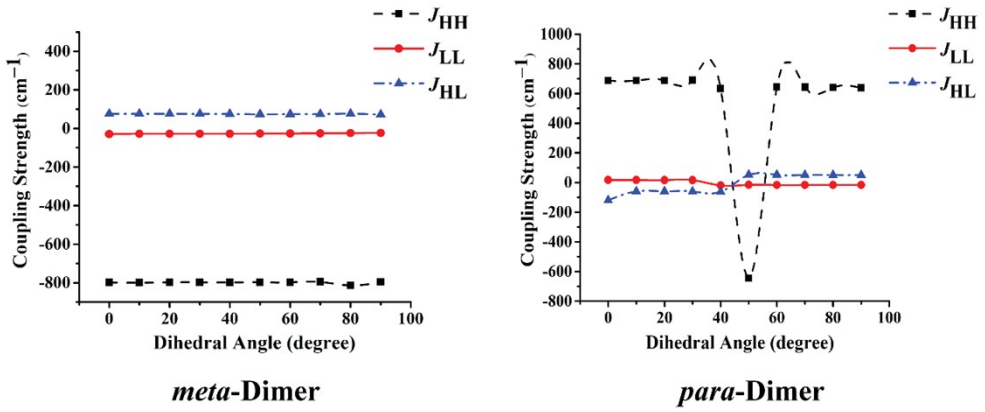


Fig. S37 The variation of coupling strengths between the HOMOs, LUMOs and HOMO and LUMO of monomer 1 and monomer 2, respectively, with dihedral angle between two PMI units in *meta*- and *para*-PMI dimers.

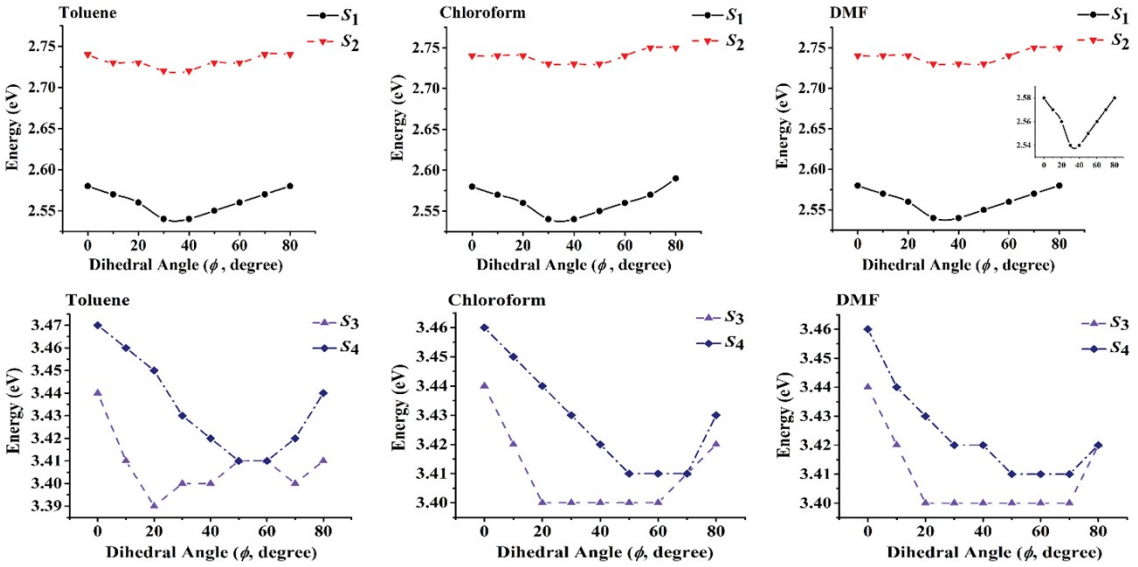
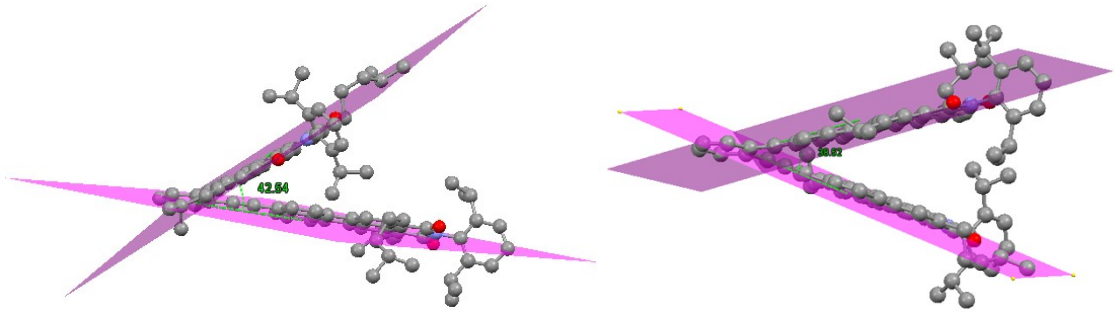


Fig. S38 Plot of TDDFT energies of lowest four excited singlet states of *ortho*-PMI dimer in toluene, DMF and chloroform versus dihedral angle.



(S_0) φ = 42.6° (S_1) φ = 38.7°

Fig. S39 The PMI-PMI dihedral angles of ground state and excited state optimized structures of *ortho*-PMI dimer.

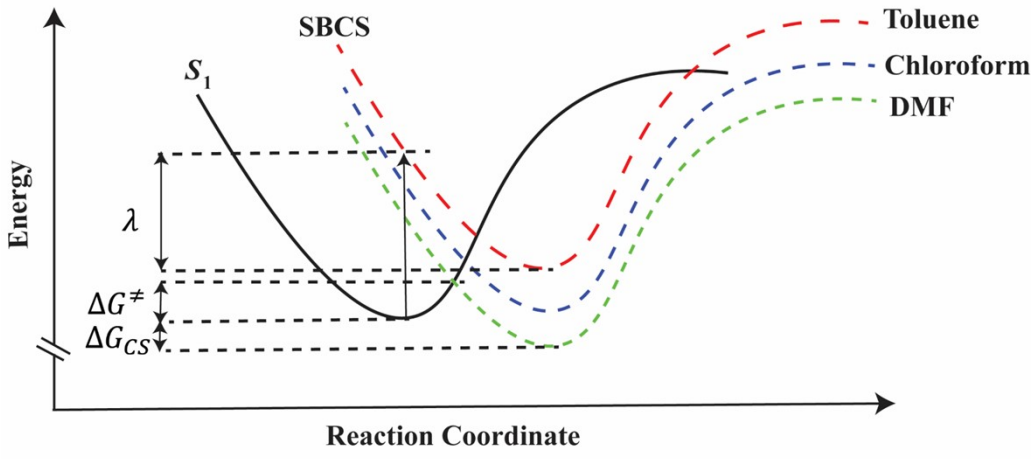


Fig. S40 A schematic diagram of SBCS process of *ortho*-PMI dimer in different solvent polarity. The axes are not scaled and in arbitrary unit.

Table S7: Calculated reorganization energies (λ_{total}) and the activation barrier ($\Delta G^{\neq}$) for the SBCS electron transfer in *ortho*-PMI dimer. All energies are in eV.

***ortho*-PMI**	ΔG_{CS}	$\lambda_{total} = (0.62 + \lambda_s)$	$\Delta G^{\neq}$
Toluene	0.46	0.63	0.47
Chloroform	0.11	0.75	0.25
DMF	– 0.19	0.84	0.13

Optimized S_0 Coordinates

PMI-monomer

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C	8.59391	3.65550	0.05854
C	7.53027	3.06836	0.05341
C	6.28878	2.36384	0.04738
C	5.03763	3.07078	0.04992
C	6.27992	0.97203	0.03878
C	3.80823	2.33100	0.04387
C	5.07516	0.25900	0.03309
H	7.22870	0.43289	0.03642
C	3.83557	0.89966	0.03580
H	5.13114	-0.82880	0.02618
C	2.58364	4.43192	0.05401
C	4.99965	4.48734	0.05825
C	3.79087	5.15205	0.06022
H	1.65066	4.99427	0.05567
H	3.76459	6.24411	0.06660
H	5.94171	5.03742	0.06299
C	2.57016	0.14938	0.03022
C	2.54856	-1.24083	0.02558
C	1.32862	0.85197	0.03095
C	1.36671	-2.00150	0.01716
H	3.49097	-1.77771	0.02831
C	0.09775	0.11602	0.02414
C	0.13315	-1.31635	0.01370
C	-1.14697	0.82530	0.02928
C	-1.16505	2.23599	0.03824
C	-2.41731	0.06782	0.02775
C	1.29961	2.27801	0.03948
C	2.56203	3.03804	0.04596
C	0.06497	2.91659	0.04215
C	-1.13590	-2.07679	-0.00128
O	-3.52711	0.57795	0.03908
O	-1.21012	-3.29624	-0.02092
N	-2.31791	-1.32875	0.00982
C	-3.56021	-2.06707	0.00431
C	-4.12864	-2.44257	1.23232
C	-4.15766	-2.37671	-1.22826
C	-5.33681	-3.15089	1.20474
C	-5.36548	-3.08600	-1.20992
C	-5.95211	-3.47020	-0.00489

H	-5.80214	-3.45682	2.14475
H	-5.85315	-3.34158	-2.15363
H	-6.89487	-4.02349	-0.00859
C	-3.46558	-2.10882	2.55858
H	-2.55381	-1.53253	2.34383
C	-4.36641	-1.21640	3.42504
H	-4.64400	-0.30130	2.87957
H	-5.29543	-1.73700	3.70950
H	-3.84895	-0.92626	4.35426
C	-3.02890	-3.38616	3.29230
H	-3.89771	-4.00642	3.56789
H	-2.36865	-3.99191	2.65288
H	-2.48710	-3.13815	4.21999
C	-3.52512	-1.97306	-2.54993
H	-2.61094	-1.40406	-2.32619
C	-4.44756	-1.04342	-3.35204
H	-5.37907	-1.55467	-3.64522
H	-4.71932	-0.15907	-2.75546
H	-3.94959	-0.70333	-4.27495
C	-3.09899	-3.20982	-3.35592
H	-2.41919	-3.84177	-2.76407
H	-3.97058	-3.82231	-3.63997
H	-2.58203	-2.91242	-4.28325
C	1.47315	-3.51302	0.01570
H	0.89391	-3.90252	0.86776
H	0.91915	-3.90084	-0.85380
C	2.88063	-4.10828	0.03491
H	3.45201	-3.75165	-0.83845
H	3.43129	-3.76314	0.92893
C	2.84737	-5.63800	0.03626
H	2.34908	-5.99390	-0.88520
H	2.20728	-5.97602	0.87079
C	4.21961	-6.32014	0.16035
C	5.14637	-5.99207	-1.01634
H	4.69531	-6.31758	-1.97012
H	5.35427	-4.91376	-1.09620
H	6.11494	-6.50762	-0.91328
C	-2.44563	3.04586	0.04520
H	-3.06054	2.73330	-0.81366
H	-3.05319	2.72869	0.90762
C	-2.30522	4.56794	0.04668
H	-1.73587	4.90079	0.93363
H	-1.72586	4.89290	-0.83386
C	-3.67033	5.25954	0.04758
H	-4.26513	4.86547	0.89087
H	-4.22451	4.97460	-0.86663
C	-3.62927	6.79299	0.14935
H	-3.06549	7.04957	1.06737
C	-2.91028	7.44150	-1.03923
H	-1.86062	7.11853	-1.11853
H	-3.41282	7.18216	-1.98745
H	-2.91203	8.54008	-0.95154
C	-5.04593	7.35838	0.29768
H	-5.56098	6.92851	1.17209
H	-5.03195	8.45388	0.41719

H	-5.65470	7.12780	-0.59369
H	4.69634	-5.93785	1.08380
C	4.05464	-7.83605	0.31147
H	5.02789	-8.33525	0.44625
H	3.42172	-8.08826	1.17774
H	3.57897	-8.26881	-0.58565
H	0.03725	4.00082	0.04870
H	9.53586	4.17115	0.06309

***ortho*-Dimer (S_0)** **212**	***meta*-Dimer (S_0)** **212**	***para*-Dimer (S_0)** **212**
C 2.00602 1.35021 -1.34271	C 4.86835 -0.41464 -0.18786	C -7.54660 2.36250 -0.64207
C 3.31596 1.52109 -0.90235	C 6.07423 0.28522 -0.19343	C -8.29530 1.21124 -0.40199
C 3.74019 2.82816 -0.50030	C 6.04155 1.71094 -0.33371	C -7.60527 -0.02138 -0.16301
C 2.80388 3.91311 -0.53947	C 4.77742 2.37748 -0.45934	C -6.17165 -0.04373 -0.19824
C 1.48362 3.68016 -0.99040	C 3.58361 1.61549 -0.44484	C -5.46248 1.15520 -0.45369
C 1.09673 2.41861 -1.38769	C 3.63266 0.24310 -0.31177	C -6.14191 2.33686 -0.66767
H 1.66185 0.37671 -1.67130	H 4.86457 -1.49927 -0.08643	H -8.04654 3.31498 -0.81391
C 5.08471 3.05824 -0.06819	C 7.25514 2.47030 -0.35057	C -8.33297 -1.22380 0.10973
C 3.22111 5.22612 -0.12760	C 4.74033 3.80945 -0.59955	C -5.47490 -1.28420 0.02377
H 0.08372 2.24516 -1.73873	H 2.70983 -0.34144 -0.30212	H -5.59113 3.26039 -0.86021
C 4.53601 5.41288 0.28957	C 5.94203 4.51661 -0.61319	C -6.21711 -2.44150 0.25841
C 5.44246 4.35059 0.31624	C 7.16894 3.85686 -0.49159	C -7.61429 -2.40586 0.30168
H 4.85785 6.40121 0.60157	H 5.91918 5.60243 -0.71990	H -5.69398 -3.38580 0.41838
H 6.44963 4.56348 0.65349	H 8.07381 4.46283 -0.51004	H -8.13950 -3.34058 0.49401
C 6.04207 1.94151 -0.04550	C 8.54634 1.77873 -0.22496	C -9.80021 -1.18217 0.18567
C 4.27232 0.40152 -0.84408	C 7.37278 -0.39867 -0.06194	C -9.76815 1.22931 -0.38802
C 5.61875 0.63615 -0.43184	C 8.58063 0.35909 -0.08693	C -10.48936 0.03989 -0.07408
C 3.90501 -0.89586 -1.16994	C 7.45724 -1.77790 0.08955	C -10.48530 2.38510 -0.67571
C 7.36321 2.12065 0.34858	C 9.75005 2.47531 -0.23606	C -10.54581 -2.31065 0.51055
C 7.89621 -0.21227 0.03974	C 11.05354 0.45402 0.00017	C -12.64103 -1.12206 0.31183
C 6.55381 -0.44964 -0.39663	C 9.84283 -0.31166 0.02964	C -11.92181 0.07162 -0.02036
C 6.13016 -1.75918 -0.79724	C 9.87224 -1.73639 0.17551	C -12.61007 1.29581 -0.30170
C 4.79243 -1.98551 -1.16338	C 8.67118 -2.47595 0.21172	C -11.88875 2.45790 -0.64826
C 8.30796 1.08516 0.40990	C 11.00815 1.85854 -0.12891	C -11.94909 -2.32104 0.58604
C 7.10769 -2.87095 -0.81852	C 11.17333 -2.43063 0.28661	C -14.08612 1.33678 -0.22179
C 8.84800 -1.34286 0.11626	C 12.35687 -0.23887 0.09975	C -14.11875 -1.09044 0.36658
N 8.38991 -2.59455 -0.32427	N 12.32130 -1.63260 0.22417	N -14.73230 0.14191 0.11693
O 6.86504 -3.99897 -1.23690	O 11.30215 -3.63820 0.41943	O -14.76158 2.33326 -0.42782
O 9.99892 -1.24895 0.53125	O 13.44153 0.32264 0.07761	O -14.82075 -2.05849 0.61804
H 7.69367 3.10863 0.63070	H 9.72727 3.55513 -0.33461	H -10.02471 -3.23808 0.72283
H 2.88080 -1.11091 -1.45171	H 6.54069 -2.35720 0.11672	H -9.94106 3.28606 -0.93806
H 0.78761 4.51193 -1.02588	H 2.62910 2.13454 -0.54217	H -4.37251 1.12458 -0.47836
C 2.32076 6.32282 -0.14155	C 3.50536 4.50155 -0.71955	C -4.05648 -1.33104 0.00819
C 1.55744 7.27208 -0.14875	C 2.45085 5.10744 -0.81816	C -2.83570 -1.35764 -0.00401
C 0.71852 8.41779 -0.18006	C 1.22157 5.82119 -0.92431	C -1.41451 -1.36006 -0.01610
C 1.29798 9.70105 -0.22056	C 1.21713 7.21704 -1.14010	C -0.68575 -2.57089 -0.03089
C -0.70278 8.30188 -0.18591	C -0.00612 5.14433 -0.80479	C -0.69863 -0.14086 -0.01309
C 0.50826 10.84355 -0.27604	C 0.00971 7.90865 -1.22858	C 0.70227 -2.56301 -0.04521
C -1.48121 9.47429 -0.24751	C -1.22571 5.84065 -0.89078	C 0.68832 -0.13302 -0.02297
C -0.88612 10.72964 -0.29274	C -1.20561 7.23642 -1.10452	C 1.41760 -1.34405 -0.04047
H -1.50726 11.61953 -0.33745	C 8.63205 -3.98183 0.37489	C -12.55766 3.77299 -0.99296
C 9.33783 -3.69566 -0.28792	H 9.23150 -4.43461 -0.43113	H -13.29820 3.58690 -1.78673
C 9.40899 -4.48838 0.87038	H 9.19940 -4.24841 1.28034	H -13.18572 4.07991 -0.14146
C 10.15099 -3.92995 -1.40998	C 12.24945 2.72694 -0.15606	C -12.64967 -3.61119 0.96070

C 10.32960 -5.54261 0.88340	H 12.83887 2.51900 0.75116	H -13.30914 -3.41065 1.81991
C 11.05545 -4.99617 -1.34829	H 12.90868 2.36866 -0.96235	H -13.36230 -3.86665 0.16071
C 11.14662 -5.79718 -0.21391	C 7.25277 -4.63825 0.41883	C -11.64744 4.92836 -1.40843
H 10.40723 -6.17152 1.76617	H 6.65508 -4.21930 1.24877	H -10.94257 5.17832 -0.59474
H 11.69669 -5.20103 -2.20132	H 6.69867 -4.41258 -0.50793	H -11.03069 4.62739 -2.27200
H 11.85552 -6.62074 -0.18498	C 7.35297 -6.15447 0.59892	C -12.45432 6.17948 -1.76311
C 10.07834 -3.07103 -2.66694	H 7.96804 -6.36472 1.49198	H -13.10778 6.43149 -0.90886
C 8.53255 -4.23394 2.09124	H 7.90752 -6.58861 -0.25435	H -13.13729 5.94700 -2.60189
C 7.61550 -5.43553 2.38791	C 6.00777 -6.88446 0.74572	C -11.61949 7.41807 -2.12711
H 6.99904 -5.67833 1.51593	H 5.47259 -6.42303 1.59830	H -10.93200 7.61585 -1.28176
H 8.19398 -6.32891 2.65116	C 6.23258 -8.36322 1.07908	C -12.52331 8.64488 -2.29053
H 6.95015 -5.21076 3.23038	H 6.83675 -8.48220 1.99307	H -13.11089 8.83596 -1.37789
C 9.38054 -3.84537 3.31745	H 5.27752 -8.89115 1.23339	H -11.93619 9.55102 -2.51151
H 10.04594 -4.66234 3.62099	H 6.76679 -8.87267 0.25845	H -13.23620 8.49889 -3.12056
H 9.99965 -2.96950 3.09734	C 5.12278 -6.73856 -0.49759	C -10.76854 7.20341 -3.38415
H 8.73411 -3.60800 4.17122	H 4.87223 -5.68750 -0.70951	H -10.04728 6.37988 -3.26553
C 9.64758 -3.90042 -3.89140	H 5.63109 -7.14747 -1.38834	H -11.40871 6.96545 -4.25160
H 10.38568 -4.67416 -4.13385	H 4.17406 -7.28583 -0.37504	H -10.19475 8.11076 -3.63334
H 8.68844 -4.39471 -3.70538	C 12.03765 4.23413 -0.29468	C -11.76496 -4.81826 1.26946
H 9.54077 -3.25573 -4.77230	H 11.49566 4.46128 -1.23095	H -11.14059 -5.07358 0.39384
C 11.40544 -2.32935 -2.91637	H 11.40284 4.60244 0.52875	H -11.06734 -4.57242 2.08766
H 11.67810 -1.72068 -2.04787	C 13.36624 4.99301 -0.29547	C -12.59880 -6.04192 1.65559
H 12.22701 -3.02931 -3.10950	H 13.88148 4.82616 0.66932	H -13.17627 -5.81480 2.57161
H 11.31822 -1.67016 -3.78871	H 14.02538 4.55260 -1.06474	H -13.35099 -6.22142 0.86673
C -2.62015 4.73606 0.09484	C 13.25777 6.50532 -0.54932	C -11.80056 -7.33665 1.87774
C -3.99596 4.59642 -0.30127	H 12.75254 6.64219 -1.52523	H -11.24412 -7.54801 0.94394
C -1.95544 3.62942 0.61647	C 12.41975 7.22141 0.51631	C -10.77821 -7.20821 3.01302
C -4.65100 3.32995 -0.15065	H 11.38178 6.85504 0.54516	H -10.02363 -6.43282 2.80870
C -4.71156 5.69010 -0.84143	H 12.85489 7.07322 1.52013	H -11.27900 -6.94639 3.96162
C -2.60008 2.39668 0.74713	H 12.38181 8.30643 0.32697	H -10.24121 -8.15752 3.17126
H -0.92002 3.72792 0.92429	C 14.65266 7.13147 -0.65219	C -12.74901 -8.51237 2.13498
C -3.93042 2.20954 0.37208	H 15.25434 6.64684 -1.43816	H -13.46883 -8.63781 1.30984
C -6.02594 3.20079 -0.52937	H 14.59561 8.20742 -0.88390	H -12.19610 -9.45888 2.24935
C -6.02810 5.54385 -1.21831	H 15.19995 7.02359 0.30020	H -13.32850 -8.35079 3.06043
H -4.20238 6.64100 -0.95679	C 13.59375 -2.31385 0.30094	C -16.17453 0.18244 0.20344
H -2.02684 1.57732 1.16389	C 14.21648 -2.44848 1.55239	C -16.76960 0.42804 1.45207
C -6.67815 4.30992 -1.06190	C 14.16080 -2.81947 -0.88071	C -16.92871 -0.02568 -0.96267
H -6.57274 6.38405 -1.63945	C 15.44868 -3.11286 1.60192	C -18.16871 0.45575 1.51525
H -7.71267 4.23907 -1.37589	C 15.39153 -3.48148 -0.78479	C -18.32471 0.01513 -0.85515
C -4.60240 0.90676 0.49326	C 16.03219 -3.62731 0.44491	C -18.94142 0.25152 0.37267
C -5.97773 0.78294 0.13887	H 15.95819 -3.22957 2.56132	H -18.65991 0.63882 2.47373
C -3.93250 -0.22074 0.95249	H 15.85427 -3.88926 -1.68660	H -18.93737 -0.14095 -1.74625
C -6.63315 -0.48384 0.27655	H 16.99320 -4.14513 0.50194	H -20.03218 0.27755 0.43969
C -4.53054 -1.48259 1.09741	C 13.59549 -1.88747 2.82137	C -15.93798 0.63051 2.70857
H -2.88911 -0.13455 1.21362	H 12.62007 -1.45446 2.55559	H -14.88264 0.69231 2.40492
C -5.89137 -1.61511 0.74812	C 13.32707 -2.99433 3.85143	C -16.27664 1.95097 3.41470
C -6.70717 1.90645 -0.34680	H 14.26413 -3.46094 4.19671	H -17.30969 1.95473 3.79888
C -8.02261 -0.59741 -0.05117	H 12.81248 -2.58522 4.73646	H -15.60429 2.11258 4.27318
C -8.74497 0.52889 -0.49653	H 12.69584 -3.78456 3.41627	H -16.16853 2.80184 2.72431
C -8.05616 1.74436 -0.63500	C 14.45359 -0.74959 3.39531	C -16.07029 -0.57954 3.64780
C -8.70078 -1.90453 0.09280	H 15.44351 -1.11696 3.71272	H -17.10608 -0.68675 4.01011
C -6.56142 -2.93022 0.85699	H 14.60814 0.03435 2.63847	H -15.79686 -1.50765 3.12366
O -6.01727 -3.94800 1.27248	H 13.96632 -0.29781 4.27527	H -15.41573 -0.46465 4.52770
O -9.90258 -2.07927 -0.08630	C 13.46570 -2.68247 -2.22582	C -16.26905 -0.27922 -2.30824
C -8.55690 -4.29613 0.56107	H 12.56888 -2.06329 -2.07813	H -15.18086 -0.29781 -2.15052

C -8.60073 -5.17305 -0.54114	C 14.34745 -1.95263 -3.24913	C -16.66112 -1.65184 -2.87447
C -9.12278 -4.63158 1.80590	H 13.79976 -1.79989 -4.19362	H -16.12580 -1.85148 -3.81747
C -9.23298 -6.40997 -0.35053	H 14.65772 -0.96856 -2.86477	H -16.41359 -2.45034 -2.15808
C -9.74536 -5.87778 1.93636	H 15.25824 -2.52730 -3.48420	H -17.74143 -1.70819 -3.08613
C -9.80123 -6.76497 0.86806	C 12.99256 -4.05246 -2.73706	C -16.56168 0.86646 -3.28918
H -9.27764 -7.10613 -1.18473	H 13.84789 -4.72044 -2.93160	H -17.63774 0.93173 -3.51992
H -10.18812 -6.15500 2.88906	H 12.34409 -4.53898 -1.99287	H -16.24659 1.82935 -2.85896
H -10.28291 -7.73243 0.98414	H 12.42914 -3.94433 -3.67868	H -16.02399 0.71304 -4.23946
C -9.08604 -3.69160 3.00661	H 2.16801 7.74433 -1.23454	H -1.22889 -3.51778 -0.03318
C -8.07274 -4.89296 -1.95296	H 0.01592 8.98849 -1.39489	H 1.25595 -3.50368 -0.05840
C -9.08844 -4.08204 -2.78490	H -0.01269 4.06699 -0.63438	H -1.25167 0.80026 0.00023
H -10.06054 -4.58598 -2.81483	H -2.15037 7.77865 -1.17198	H 1.23086 0.81428 -0.02063
H -9.25129 -3.08577 -2.36509	C -2.46185 5.14329 -0.75572	C 2.83866 -1.32704 -0.05510
H -8.72947 -3.96929 -3.81557	C -3.51780 4.54426 -0.63483	C 4.05919 -1.29192 -0.06949
C -6.65783 -4.29559 -2.06270	C -4.74818 3.84906 -0.48572	C 5.47749 -1.24291 -0.08948
H -6.64222 -3.22140 -1.85700	C -5.92243 4.55046 -0.21601	C 6.17553 -0.00696 0.15235
H -5.95981 -4.78569 -1.37741	C -4.80514 2.41591 -0.60414	C 6.21828 -2.39586 -0.34911
H -6.28718 -4.43267 -3.08559	C -7.14004 3.88232 -0.05088	C 7.60902 0.01553 0.11126
C -10.50605 -3.26715 3.42797	H -5.88466 5.63754 -0.12809	C 7.61511 -2.35963 -0.39920
H -10.46049 -2.54675 4.25390	C -6.05955 1.74097 -0.43506	H 5.69405 -3.33702 -0.52334
H -11.03447 -2.80118 2.59002	C -7.24371 2.49335 -0.14885	C 8.33484 -1.18133 -0.18916
H -11.09844 -4.12487 3.76797	H -8.02295 4.48391 0.16120	H 8.13917 -3.29066 -0.61151
C -8.30097 -4.30725 4.18052	C -6.11236 0.31449 -0.55846	C 7.55397 2.38976 0.63614
H -7.28581 -4.57329 3.86902	C -4.93520 -0.37766 -0.83989	C 5.46813 1.18735 0.43323
H -8.23420 -3.59398 5.01117	C -7.40159 -0.37806 -0.38848	C 6.14928 2.36450 0.66611
H -8.78785 -5.21328 4.56021	C -3.70898 0.28857 -1.00505	H 8.05541 3.33863 0.82313
N -7.90007 -3.00301 0.43694	C -3.64083 1.66169 -0.89005	H 5.59984 3.28467 0.87768
H -8.62118 2.59638 -0.98103	C -8.57858 0.37245 -0.09665	H 4.37820 1.15687 0.46186
H -2.56255 9.37976 -0.25061	C -8.52391 1.79258 0.02984	C 9.80141 -1.13803 -0.27368
H 0.97758 11.82251 -0.30894	H -2.69414 2.18773 -1.02015	C 10.54446 -2.25958 -0.62647
H 2.38040 9.78082 -0.21402	H -2.80921 -0.28963 -1.22750	C 10.49273 0.07722 0.01003
C 4.20802 -3.32125 -1.57868	H -4.94760 -1.46232 -0.93970	C 11.94745 -2.27043 -0.70722
H 4.65876 -4.13384 -1.00843	C -9.83055 -0.30679 0.06983	H 10.02101 -3.18138 -0.85608
H 3.13632 -3.29894 -1.34546	C -9.88311 -1.73148 -0.07039	C 11.92481 0.10910 -0.05112
C 9.72263 1.40948 0.86851	C -11.00872 0.45097 0.37036	C 12.64167 -1.07740 -0.41326
H 9.95357 0.79255 1.74424	C -11.17836 -2.43047 0.07431	C 12.61527 1.32566 0.25621
H 10.42508 1.04679 0.10982	C -12.29966 -0.24926 0.54859	C 11.89713 2.47722 0.64234
C 10.03736 2.87794 1.18745	C -9.69783 2.48076 0.31798	C 14.09022 1.37019 0.16111
H 9.84374 3.51068 0.30883	C -10.94414 1.85533 0.49300	C 9.77389 1.25928 0.35567
H 9.37848 3.23990 1.98741	C -7.50626 -1.75908 -0.50547	C 8.30099 1.24263 0.37223
C 11.50358 3.05360 1.61083	C -8.71257 -2.46504 -0.35765	C 10.49360 2.40557 0.67351
H 12.14671 2.62587 0.82846	H -6.61323 -2.33315 -0.72671	C 14.11918 -1.04498 -0.47568
H 11.69463 2.45824 2.51659	H -9.65988 3.56033 0.41605	O 14.76614 2.36459 0.37555
C 11.94334 4.50924 1.86497	N -12.29308 -1.63777 0.36887	O 14.81920 -2.00772 -0.75158
H 11.70873 5.09126 0.95965	O -13.35229 0.30286 0.82903	N 14.73451 0.18210 -0.20425
C 13.46218 4.57885 2.08471	O -11.32878 -3.63667 -0.05030	C 16.17640 0.22476 -0.29643
H 13.79667 5.61333 2.22718	C -12.15498 2.71410 0.79745	C 16.76686 0.48969 -1.54330
H 13.75552 4.00944 2.97638	H -12.94009 2.47976 0.06158	C 16.93506 0.00119 0.86407
H 14.00941 4.16299 1.23039	H -12.59854 2.36791 1.74464	C 18.16572 0.52005 -1.61088
C 11.20055 5.15388 3.04562	C -11.93924 4.22633 0.84835	C 18.33060 0.04589 0.75238
H 10.11768 5.19100 2.88385	H -11.20786 4.48634 1.63529	C 18.94270 0.30046 -0.47410
H 11.38049 4.59278 3.97228	H -11.50754 4.57582 -0.10450	H 18.65330 0.71800 -2.56825
H 11.54397 6.18223 3.20957	C -13.24798 4.97140 1.12071	H 18.94660 -0.12156 1.63910
C 4.39548 -3.60922 -3.08530	H -13.71313 4.54976 2.02957	H 20.03318 0.32927 -0.54446
H 5.46149 -3.52956 -3.31963	H -13.96003 4.76621 0.29916	C 15.93096 0.71091 -2.79375

H 3.88541 -2.83135 -3.66932	C -13.11429 6.49265 1.29750	H 14.87657 0.76712 -2.48561
C 3.91432 -5.00634 -3.50986	H -12.41578 6.66904 2.13845	C 16.26619 2.04245 -3.48050
H 4.15931 -5.14704 -4.57351	C -12.53500 7.18026 0.05562	H 16.16061 2.88262 -2.77674
H 4.50567 -5.75253 -2.96107	H -11.52039 6.82500 -0.18228	H 17.29763 2.05266 -3.86885
C 2.41661 -5.31953 -3.31308	H -13.17120 6.99284 -0.82717	H 15.59029 2.21700 -4.33364
H 2.17551 -5.20213 -2.24596	H -12.47760 8.27156 0.19829	C 16.06172 -0.48405 -3.75233
C 2.12884 -6.78137 -3.68838	C -14.46603 7.10823 1.67439	H 17.09635 -0.58343 -4.12018
H 2.34639 -6.96338 -4.74916	H -14.87883 6.64794 2.58682	H 15.79202 -1.42060 -3.24154
H 2.74399 -7.47266 -3.10021	H -14.37933 8.19259 1.85143	H 15.40359 -0.35658 -4.62783
H 1.07657 -7.03786 -3.51658	H -15.20215 6.96041 0.86517	C 16.28054 -0.26854 2.20908
C 1.50804 -4.37080 -4.10952	C -8.69704 -3.97243 -0.51274	H 15.19227 -0.29704 2.05322
H 0.45130 -4.62709 -3.96742	H -9.13342 -4.42022 0.39421	C 16.56394 0.87415 3.19649
H 1.63697 -3.32477 -3.80897	H -9.42211 -4.24924 -1.29430	H 17.63981 0.94735 3.42579
H 1.72332 -4.43524 -5.18447	C -7.34715 -4.62496 -0.80956	H 16.23993 1.83663 2.77216
C -3.68656 -2.64610 1.60317	H -6.92426 -4.20874 -1.73942	H 16.02898 0.71028 4.14659
H -4.20803 -3.11053 2.44441	H -6.62341 -4.39190 -0.00732	C 16.68702 -1.64027 2.76692
H -3.69585 -3.42769 0.83461	C -7.46964 -6.14485 -0.93864	H 16.44800 -2.43734 2.04602
C -10.22760 0.48576 -0.83918	H -7.96917 -6.53768 -0.03514	H 17.76770 -1.68683 2.97896
H -10.39078 -0.30181 -1.58347	H -8.14419 -6.38699 -1.78134	H 16.15360 -1.85098 3.70857
H -10.77529 0.12367 0.03791	C -6.14106 -6.89446 -1.13014	C 12.64360 -3.55595 -1.10647
C -10.87195 1.78856 -1.33404	H -5.48777 -6.63371 -0.27487	H 13.29200 -3.34626 -1.97202
H -10.75675 2.57669 -0.57865	C -5.41461 -6.48381 -2.41641	H 13.36595 -3.82069 -0.31835
H -10.36551 2.14598 -2.24266	H -6.04498 -6.68120 -3.30114	C 11.75211 -4.75923 -1.41085
C -12.36295 1.58835 -1.64502	H -5.15415 -5.41398 -2.42413	H 11.12042 -4.98970 -0.53668
H -12.88671 1.27535 -0.72903	H -4.47883 -7.05232 -2.54135	H 11.06086 -4.52438 -2.24084
H -12.46350 0.75086 -2.35013	C -6.37071 -8.40920 -1.09885	C 12.57428 -5.99438 -1.78442
C -13.08039 2.81726 -2.23823	H -5.42141 -8.96222 -1.18633	H 13.22533 -6.26994 -0.93342
H -12.51856 3.13224 -3.13186	H -6.86065 -8.72296 -0.16280	H 13.25911 -5.72883 -2.60945
C -14.50091 2.44256 -2.68734	H -7.01867 -8.72400 -1.93508	C 11.75193 -7.22427 -2.20253
H -15.10812 2.11507 -1.83330	C -13.56520 -2.31511 0.48003	C 10.81639 -7.71001 -1.08901
H -15.01083 3.29682 -3.14840	C -14.37056 -2.42243 -0.66591	H 11.38979 -7.96929 -0.18183
H -14.48695 1.62488 -3.41772	C -13.95078 -2.84172 1.72339	H 10.07374 -6.94732 -0.80791
C -13.12159 4.00510 -1.26428	C -15.59721 -3.08760 -0.54410	H 10.26269 -8.61037 -1.40092
H -13.65033 3.73360 -0.34088	C -15.18422 -3.50142 1.79996	C 12.56996 3.77865 1.02878
H -12.11908 4.34762 -0.98536	C -16.00197 -3.62428 0.67735	H 13.32190 3.56148 1.80357
H -13.64871 4.85766 -1.70884	H -16.24379 -3.18715 -1.41922	H 13.18482 4.12068 0.18107
C -2.23090 -2.34845 2.00341	H -15.50818 -3.92633 2.75287	C 11.66431 4.91404 1.50509
H -1.70850 -1.85343 1.17460	H -16.96149 -4.14217 0.75514	H 10.95638 5.20522 0.70790
H -1.72797 -3.31833 2.11034	C -13.06132 -2.73087 2.95071	H 11.05102 4.57161 2.35547
C -2.04440 -1.54341 3.31586	H -12.20580 -2.09087 2.68885	C 12.47580 6.14353 1.91980
H -1.26661 -0.78097 3.16952	C -13.94035 -1.84618 -2.00528	H 13.13925 6.42858 1.08386
H -2.96448 -0.98984 3.55275	H -12.96406 -1.36037 -1.86433	H 13.14914 5.86995 2.75397
C -1.64644 -2.38407 4.54795	C -13.78782 -2.05014 4.11941	C 11.64586 7.37098 2.32993
H -0.72340 -2.92647 4.28922	H -14.16922 -1.06228 3.81776	H 10.98665 7.62627 1.47753
C -2.71002 -3.42422 4.92957	H -14.64185 -2.65108 4.47198	C 10.75388 7.09695 3.54655
H -3.66136 -2.93776 5.18228	H -13.10444 -1.91357 4.97350	H 10.02257 6.29624 3.35609
H -2.90340 -4.13488 4.11895	C -12.49626 -4.10701 3.33839	H 11.36290 6.79451 4.41638
H -2.39187 -4.00326 5.80473	H -11.96287 -4.55787 2.48796	H 10.18854 7.99832 3.83380
C -1.33349 -1.47026 5.74197	H -11.79729 -4.01864 4.18672	C 12.56058 8.57220 2.59186
H -1.00541 -2.05190 6.61154	H -13.30283 -4.79677 3.63742	H 13.18373 8.80373 1.71281
H -0.54109 -0.75135 5.50075	C -13.74169 -2.95687 -3.04791	H 11.97920 9.47431 2.84242
H -2.22174 -0.89878 6.04197	H -13.02013 -3.70459 -2.68433	H 13.24014 8.36751 3.43719
C -1.34532 7.03653 -0.11355	H -14.68885 -3.47766 -3.26432	H 11.12414 -6.92569 -3.06449
C -1.94230 5.97771 -0.02656	H -13.36473 -2.53860 -3.99584	C 12.67600 -8.35563 -2.66504
H 9.30964 -2.30763 -2.51240	C -14.91656 -0.76260 -2.48664	H 12.10053 -9.22688 -3.01768

H 7.88193 -3.38227 1.87004 H -8.01200 -5.88315 -2.42377 H -8.55698 -2.77996 2.71463	H -15.02196 0.02851 -1.72833 H -14.55746 -0.30411 -3.42274 H -15.91757 -1.18046 -2.68287	H 13.33357 -8.02873 -3.48689 H 13.32238 -8.69538 -1.83742 H 9.95143 3.29891 0.96483

Optimized S_1 Coordinates

PMI-monomer

C	8.56819	3.63914	0.18248
C	7.50380	3.06142	0.15680
C	6.26318	2.36402	0.12701
C	5.01665	3.06731	0.13992
C	6.25900	0.96349	0.08488
C	3.79157	2.32690	0.11141
C	5.07540	0.25211	0.05694
H	7.21270	0.43413	0.07457
C	3.81717	0.90261	0.07009
H	5.12800	-0.83412	0.02461
C	2.56218	4.43648	0.16632
C	4.97056	4.47446	0.18039
C	3.75551	5.14384	0.19327
H	1.62717	4.99274	0.17961
H	3.73689	6.23488	0.22537
H	5.90802	5.03135	0.20177
C	2.57738	0.16540	0.04349
C	2.56018	-1.24612	0.00296
C	1.33984	0.86029	0.06195
C	1.39614	-1.99475	-0.03336
H	3.50579	-1.77639	-0.00231
C	0.11195	0.12354	0.04404
C	0.15046	-1.29951	-0.01844
C	-1.12560	0.83024	0.08845
C	-1.15267	2.25407	0.10248
C	-2.38930	0.06957	0.13820
C	1.30955	2.27470	0.09889
C	2.54887	3.02533	0.12494
C	0.05869	2.92668	0.10438
C	-1.11469	-2.05316	-0.07963
O	-3.48812	0.58036	0.26290
O	-1.18665	-3.26222	-0.21116
N	-2.29546	-1.31673	0.03222
C	-3.53406	-2.06026	0.04080
C	-4.05751	-2.49032	1.26798
C	-4.17485	-2.32661	-1.17700
C	-5.25689	-3.20412	1.25320
C	-5.37113	-3.04496	-1.14316
C	-5.91050	-3.48099	0.05980
H	-5.68834	-3.54871	2.19539
H	-5.89000	-3.26821	-2.07778
H	-6.84804	-4.04143	0.06728
C	-3.37364	-2.19036	2.59065
H	-2.42832	-1.67520	2.37090
C	-4.21888	-1.23635	3.44060
H	-4.43907	-0.31378	2.88436

H	-5.17757	-1.69758	3.72515
H	-3.68974	-0.96750	4.36824
C	-3.01740	-3.47223	3.34858
H	-3.91805	-4.03418	3.64064
H	-2.39336	-4.13273	2.72901
H	-2.46258	-3.23567	4.26979
C	-3.60169	-1.87567	-2.50924
H	-2.70416	-1.27630	-2.30287
C	-4.57718	-0.97288	-3.26909
H	-5.49394	-1.51336	-3.55106
H	-4.86973	-0.10873	-2.65484
H	-4.11629	-0.59849	-4.19645
C	-3.15624	-3.07701	-3.34930
H	-2.43633	-3.69336	-2.79189
H	-4.01229	-3.71534	-3.61860
H	-2.68068	-2.74388	-4.28505
C	1.49184	-3.50466	-0.07738
H	0.87895	-3.91654	0.73778
H	0.97304	-3.86133	-0.97929
C	2.89065	-4.10873	-0.01937
H	3.49452	-3.74234	-0.86516
H	3.41047	-3.78258	0.89853
C	2.84729	-5.63461	-0.04550
H	2.37776	-5.97157	-0.98742
H	2.17765	-5.98059	0.76031
C	4.20308	-6.33215	0.11301
C	5.16599	-6.01144	-1.02997
H	4.74364	-6.33082	-1.99725
H	5.38657	-4.93637	-1.10122
H	6.12496	-6.53542	-0.89768
C	-2.43824	3.05337	0.10729
H	-3.07678	2.69228	-0.71207
H	-3.01400	2.78458	1.00522
C	-2.30405	4.56940	0.01478
H	-1.73306	4.95853	0.87588
H	-1.72958	4.83892	-0.88626
C	-3.66681	5.25663	-0.01873
H	-4.25076	4.92323	0.85607
H	-4.23057	4.90804	-0.90294
C	-3.62874	6.78906	-0.02612
H	-3.04252	7.11063	0.85464
C	-2.94735	7.35297	-1.27265
H	-1.90149	7.02488	-1.36160
H	-3.47684	7.03235	-2.18522
H	-2.94667	8.45364	-1.25940
C	-5.03847	7.35944	0.11937
H	-5.52872	6.99356	1.03439
H	-5.02538	8.45934	0.15989
H	-5.66942	7.06570	-0.73558
H	4.65714	-5.96328	1.05131
C	4.01533	-7.84215	0.24887
H	4.97663	-8.35430	0.40758
H	3.35635	-8.09187	1.09441
H	3.56039	-8.26357	-0.66261
H	0.03799	4.01036	0.11336

H	9.51456	4.14738	0.20507

***ortho*-Dimer (S_1)**	***meta*-Dimer (S_1)**	***para*-Dimer (S_1)**
212	**212**	**212**
C 2.12885 1.25114 -1.38136	C 4.89360 -0.44897 0.20111	C -7.87689 2.86471 -0.43039
C 3.43522 1.44413 -0.93886	C 6.10300 0.26488 0.10519	C -8.50303 1.62732 -0.27862
C 3.82136 2.73916 -0.47844	C 6.05372 1.68302 -0.03016	C -7.69314 0.46304 -0.11643
C 2.86124 3.79746 -0.47921	C 4.78357 2.34393 -0.06614	C -6.26891 0.58905 -0.14302
C 1.55427 3.54744 -0.94019	C 3.60881 1.58120 0.03320	C -5.69185 1.86071 -0.30591
C 1.19635 2.29088 -1.38235	C 3.66840 0.20118 0.16548	C -6.48703 2.98159 -0.44170
H 1.81143 0.27545 -1.74463	H 4.90403 -1.53209 0.30364	H -8.47168 3.76972 -0.53923
C 5.15355 2.98267 -0.02775	C 7.25788 2.43969 -0.12947	C -8.29499 -0.81687 0.07137
C 3.24821 5.10645 -0.02338	C 4.73461 3.77506 -0.20254	C -5.44968 -0.58955 -0.00941
H 0.18116 2.10625 -1.73865	H 2.74642 -0.37820 0.24202	H -6.02943 3.96533 -0.56161
C 4.56489 5.31053 0.39929	C 5.94268 4.49201 -0.29115	C -6.07910 -1.83433 0.13705
C 5.48638 4.27527 0.39825	C 7.15977 3.84909 -0.25615	C -7.45666 -1.93996 0.18128
H 4.86373 6.30247 0.74028	H 5.90261 5.57733 -0.39198	H -5.46242 -2.72953 0.22558
H 6.49521 4.49410 0.74235	H 8.06154 4.45296 -0.33051	H -7.88772 -2.93184 0.30118
C 6.12773 1.89547 -0.02806	C 8.53260 1.76471 -0.10210	C -9.74365 -0.92871 0.14726
C 4.42272 0.35758 -0.94325	C 7.39277 -0.40615 0.13708	C -9.96357 1.49330 -0.28187
C 5.74875 0.60493 -0.49414	C 8.58402 0.34896 0.02591	C -10.55471 0.22614 -0.04453
C 4.09968 -0.92239 -1.36886	C 7.48854 -1.80059 0.27607	C -10.79541 2.58337 -0.51848
C 7.43215 2.08384 0.42039	C 9.74427 2.47528 -0.19936	C -10.37109 -2.14694 0.40773
C 8.02981 -0.20588 -0.01888	C 11.04710 0.45187 -0.07041	C -12.56635 -1.16959 0.25296
C 6.71071 -0.44937 -0.50448	C 9.85129 -0.31639 0.04128	C -11.97689 0.10561 0.00006
C 6.33604 -1.73656 -1.00017	C 9.89275 -1.73676 0.17042	C -12.78508 1.26335 -0.21224
C 5.01892 -1.97898 -1.41414	C 8.69575 -2.48794 0.29731	C -12.19188 2.50847 -0.49788
C 8.39688 1.07253 0.44718	C 10.99157 1.86861 -0.18516	C -11.75684 -2.30463 0.47149
C 7.34861 -2.81287 -1.07324	C 11.19807 -2.42543 0.16709	C -14.25620 1.14801 -0.11913
C 9.00743 -1.31519 0.01142	C 12.35187 -0.23615 -0.06938	C -14.03808 -1.29580 0.27857
N 8.59673 -2.54221 -0.51406	N 12.33429 -1.62769 0.03803	N -14.77856 -0.12630 0.10113
O 7.15284 -3.89779 -1.58539	O 11.33329 -3.63187 0.26290	O -15.02084 2.08829 -0.22031
O 10.13260 -1.21748 0.46146	O 13.42535 0.33223 -0.15818	O -14.63010 -2.34506 0.44661
H 7.72446 3.06446 0.77846	H 9.70798 3.55480 -0.29121	H -9.75736 -3.02442 0.57749
H 3.08483 -1.14447 -1.69416	H 6.57618 -2.37794 0.37240	H -10.34643 3.54674 -0.73398
H 0.83297 4.36575 -0.95148	H 2.64542 2.09104 0.00570	H -4.60500 1.94768 -0.32385
C 2.33205 6.17773 -0.00540	C 3.51008 4.46868 -0.25092	C -4.04625 -0.52197 -0.02451
C 1.55514 7.11934 0.00423	C 2.45857 5.08695 -0.29262	C -2.82258 -0.50185 -0.03398
C 0.70263 8.24388 -0.02782	C 1.23760 5.81081 -0.33442	C -1.41502 -0.50113 -0.04750
C 1.25932 9.53928 0.03862	C 1.23952 7.21734 -0.41883	C -0.69403 -1.72049 -0.07087
C -0.71395 8.10889 -0.15766	C 0.00723 5.13370 -0.28955	C -0.68178 0.71063 -0.03724
C 0.46355 10.66377 -0.04921	C 0.04042 7.91566 -0.45352	C 0.68208 -1.72750 -0.08775
C -1.50049 9.27926 -0.25994	C -1.20186 5.83732 -0.32553	C 0.69490 0.70342 -0.04410
C -0.92577 10.53219 -0.20740	C -1.17489 7.24094 -0.40719	C 1.41560 -0.51565 -0.07144
H -1.55401 11.42181 -0.28151	C 8.67957 -3.99388 0.45392	C -12.99512 3.75873 -0.78670
C 9.56281 -3.61710 -0.50735	H 9.21102 -4.43914 -0.40003	H -13.74477 3.51815 -1.55411
C 9.67993 -4.41197 0.64210	H 9.31851 -4.26188 1.30790	H -13.61279 3.98777 0.09472
C 10.35029 -3.83276 -1.64704	C 12.22978 2.73324 -0.28926	C -12.32267 -3.67646 0.77216
C 10.61767 -5.44582 0.62850	H 12.87663 2.51764 0.57392	H -13.01736 -3.58726 1.62018
C 11.26962 -4.88251 -1.61636	H 12.83129 2.38217 -1.14031	H -12.98438 -3.96966 -0.05629
C 11.40512 -5.68321 -0.49009	C 7.31525 -4.65762 0.60596	C -12.22006 5.00217 -1.21096
H 10.73398 -6.07699 1.51191	H 6.78571 -4.24799 1.48394	H -11.52678 5.31914 -0.41233
H 11.89170 -5.07698 -2.49250	H 6.68696 -4.43013 -0.27037	H -11.59722 4.77340 -2.09084
H 12.13134 -6.49914 -0.48390	C 7.43858 -6.17091 0.76697	C -13.15997 6.16154 -1.53302

C 10.21942 -2.97974 -2.89727	H 8.12333 -6.38085 1.60622	H -13.81361 6.33595 -0.66137
C 8.84738 -4.16276 1.88854	H 7.92677 -6.59563 -0.12887	H -13.83543 5.86412 -2.35558
C 8.07021 -5.40903 2.32120	C 6.12056 -6.91373 1.01439	C -12.47757 7.48289 -1.90526
H 7.44117 -5.78872 1.50278	H 5.64363 -6.45588 1.90074	H -11.79628 7.75113 -1.07655
H 8.74443 -6.22172 2.63243	C 6.38706 -8.38335 1.33563	C -13.51335 8.59835 -2.03620
H 7.41787 -5.17763 3.17732	H 7.05468 -8.49164 2.20400	H -14.09582 8.71896 -1.11005
C 9.71760 -3.61226 3.02394	H 5.45355 -8.92224 1.55871	H -13.03763 9.56447 -2.26399
H 10.46994 -4.35168 3.34079	H 6.86754 -8.88936 0.48215	H -14.22432 8.37752 -2.84918
H 10.24853 -2.70579 2.70118	C 5.14752 -6.78869 -0.15775	C -11.64311 7.37423 -3.18141
H 9.10127 -3.36478 3.90246	H 4.87272 -5.74376 -0.36292	H -10.83360 6.63531 -3.09085
C 9.63071 -3.79058 -4.05660	H 5.59034 -7.20473 -1.07801	H -12.27403 7.07595 -4.03524
H 10.30714 -4.60692 -4.35504	H 4.21610 -7.34082 0.04063	H -11.17948 8.34013 -3.43385
H 8.66803 -4.23513 -3.76751	C 12.01497 4.23880 -0.40021	C -11.32218 -4.79295 1.05141
H 9.47109 -3.15023 -4.93826	H 11.41342 4.47507 -1.29553	H -10.66841 -4.95183 0.17600
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H 11.41178 -1.64923 -4.14048	H 13.94021 4.55584 -1.30300	H -12.73537 -6.34359 0.57612
C -2.64100 4.56779 -0.00237	C 13.22934 6.50216 -0.71197	C -11.10111 -7.31235 1.59373
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C -4.71819 3.22257 -0.18937	H 11.47971 6.85460 0.56720	H -9.47164 -6.25862 2.62163
C -4.74223 5.58199 -0.84052	H 13.04469 7.06983 1.38289	H -10.69449 -6.95995 3.70480
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C -9.69815 -6.30708 0.35163	H 14.44501 -0.93514 -3.19804	H -15.97301 -2.91753 -2.00479
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VI. Femtosecond transient absorption study:

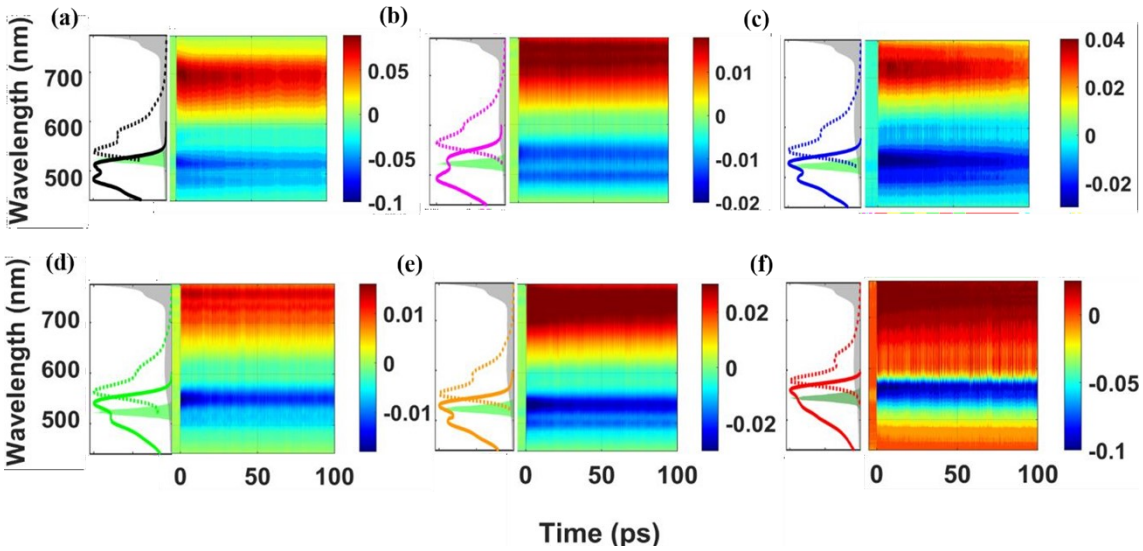

Fig. S41 2D contour plots of fs-TA data over probe delays from 0 to 100 ps, for (a) monomer, (b) *ortho*-, (c) *meta*-, (d) *para*-PMI dimers, (e) 1,3,5-PMI trimer and (f) self-coupled PMI dimer in $CHCl_3$ along with corresponding absorption (solid), emission (dashed), pump (filled, green) and probe (filled, grey) spectra.

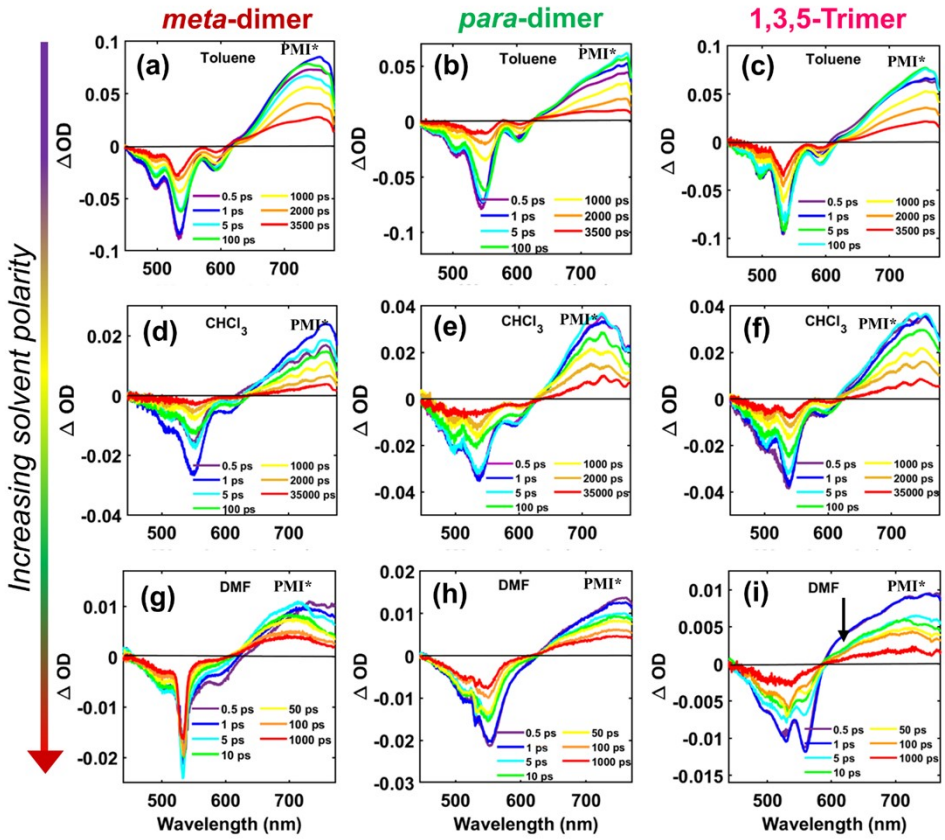

Fig. S42 Plots for transient absorption spectral traces at various probe delays of *meta*-PMI dimer (left panel), *para*-PMI dimer (middle panel), 1,3,5-PMI trimer (right panel) dimer in toluene (a, b, c), $CHCl_3$ (d, e, f), and

DMF (g, h, i), respectively.

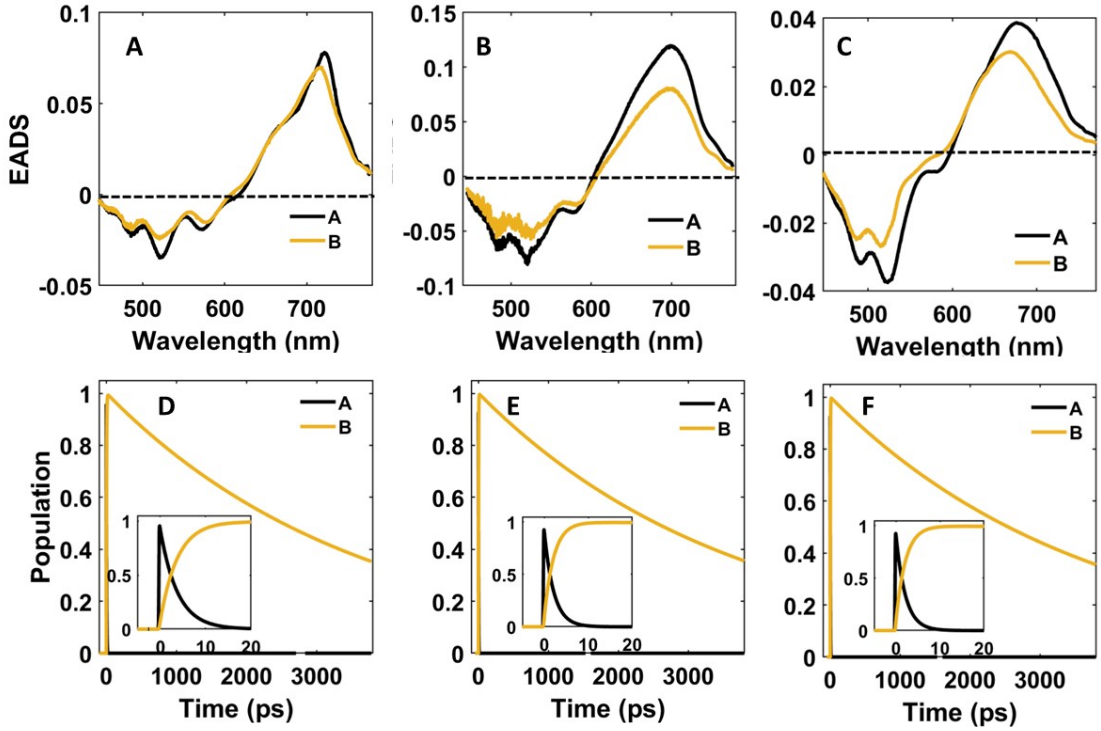

Fig. S43 Plots for global analysis fits for selected fs-TA wavelengths for ***o*-PMI-ac** monomer (λ_{ex} = 530 nm) in toluene (a, d), $CHCl_3$ (b, e), and DMF (c, f), respectively.

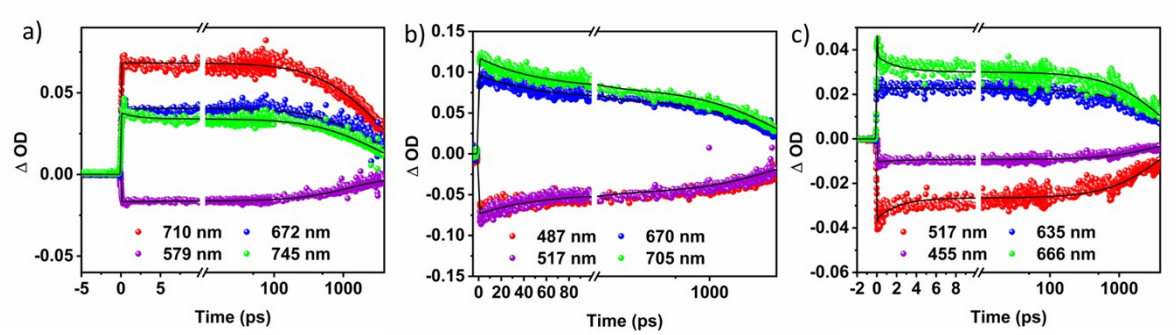

Fig. S44 Global analysis fits for selected fs-TA wavelengths for ***o*-PMI-ac** monomer in (a) toluene (b) $CHCl_3$ and (c) DMF respectively (raw data: empty circle; fitting data: solid line)

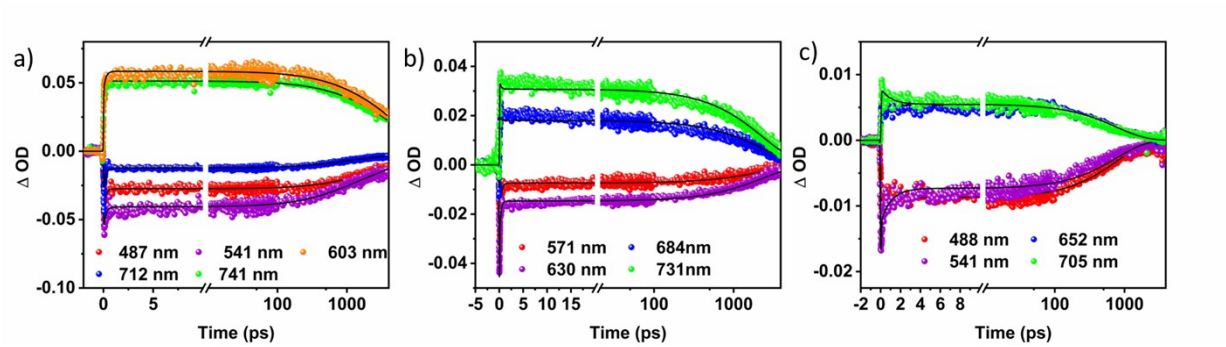

Fig. S45 Global analysis fits for selected fs-TA wavelengths for *ortho*-PMI dimer in (a) toluene (b) $CHCl_3$ and (c) DMF respectively (raw data: empty circle; fitting data: solid line).

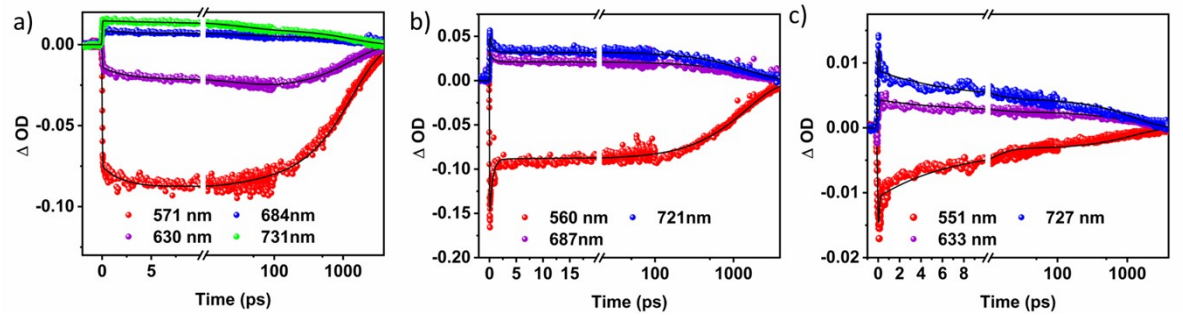

Fig. S46 Global analysis fits for selected fs-TA wavelengths for self-coupled PMI dimer in (a) toluene (b) $CHCl_3$ and (c) DMF respectively (raw data: empty circle; fitting data: solid line).

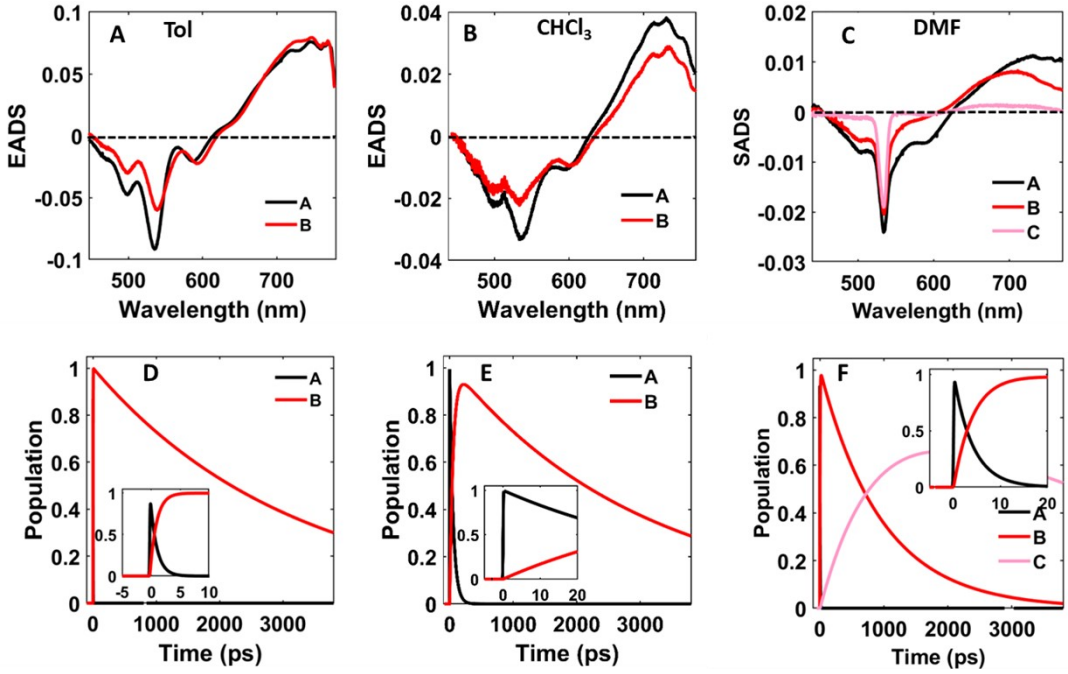

Fig. S47 Plots for global analysis fits for selected fs-TA wavelengths for *meta*-PMI dimer (λ_{ex} = 530 nm) in toluene (a, d), $CHCl_3$ (b, e), and DMF (c, f), respectively.

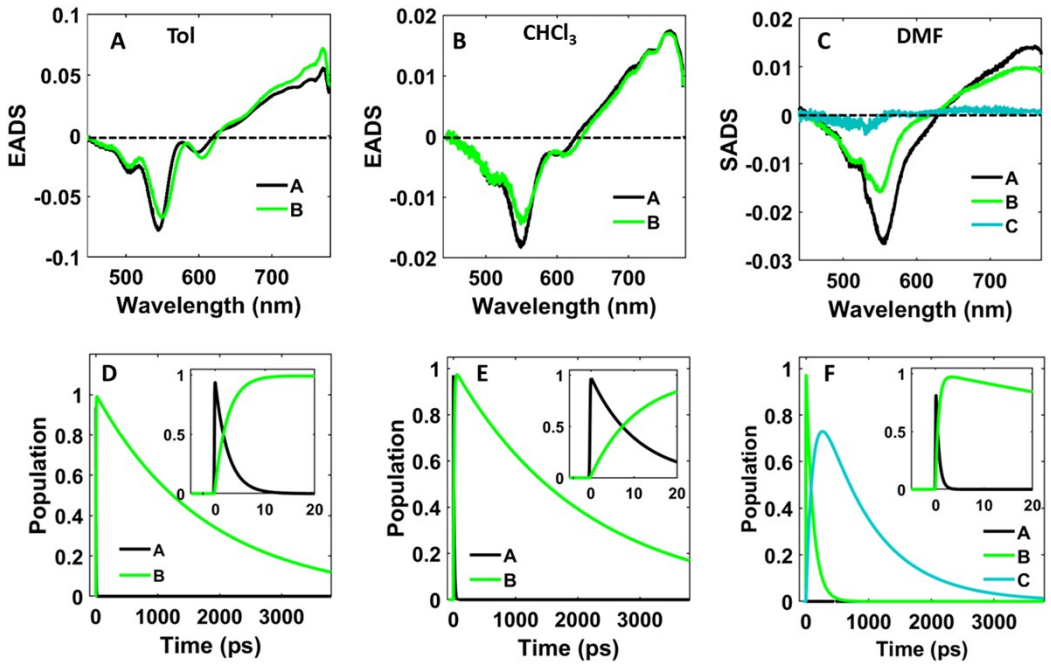

Fig. S48 Plots for global analysis fits for selected fs-TA wavelengths for *para*-PMI dimer (λ_{ex} = 530 nm) in toluene (a, d), $CHCl_3$ (b, e), and DMF (c, f), respectively.

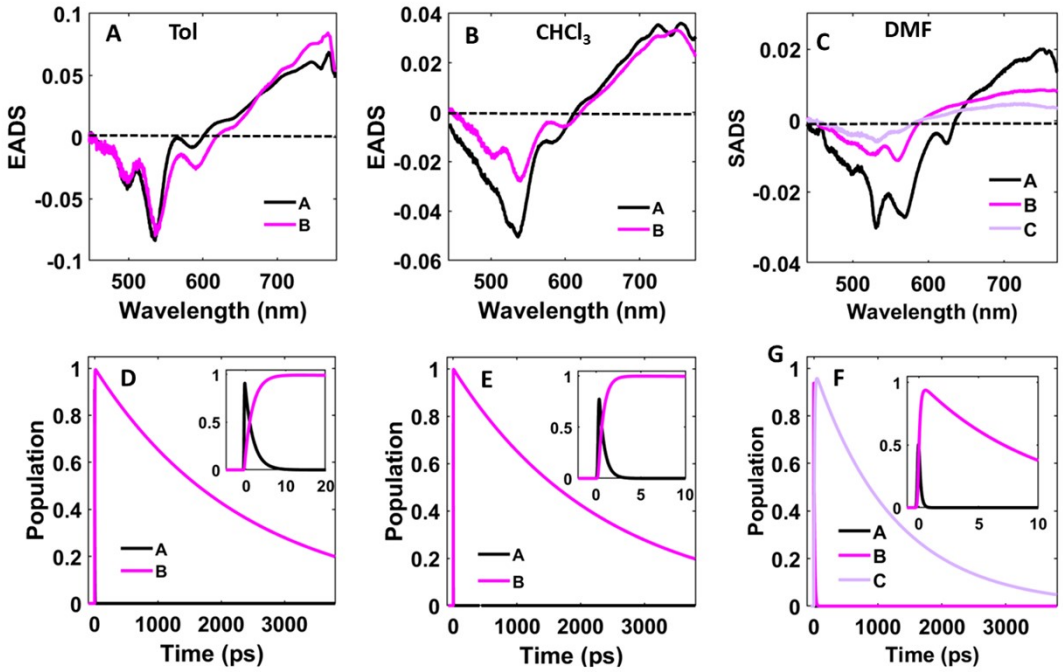

Fig. S49 Plots for global analysis fits for selected fs-TA wavelengths for 1,3,5-PMI trimer (λ_{ex} = 530 nm) in toluene (a, d), $CHCl_3$ (b, e), and DMF (c, f), respectively.

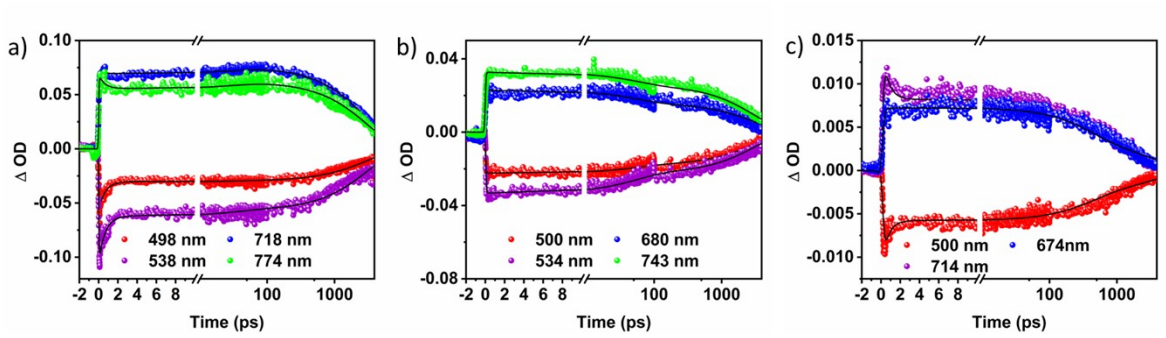

Fig. S50 Global analysis fits for selected fs-TA wavelengths for *meta*-PMI dimer in (a) toluene (b) $CHCl_3$ and (c) DMF respectively (raw data: empty circle; fitting data: solid line).

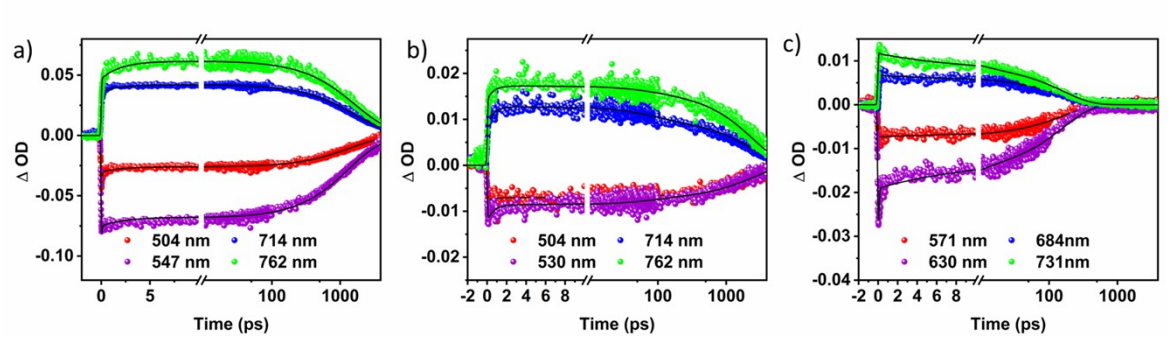

Fig. S51 Global analysis fits for selected fs-TA wavelengths for *para*-PMI dimer in (a) toluene (b) $CHCl_3$ and (c) DMF respectively (raw data: empty circle; fitting data: solid line).

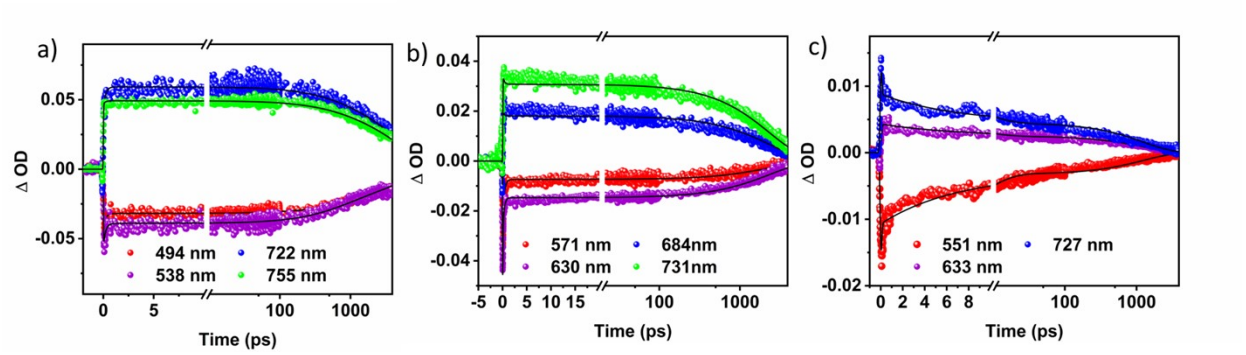

Fig. S52 Global analysis fits for selected fs-TA wavelengths for 1,3,5-PMI trimer in (a) toluene (b) $CHCl_3$ and (c) DMF respectively (raw data: empty circle; fitting data: solid line).

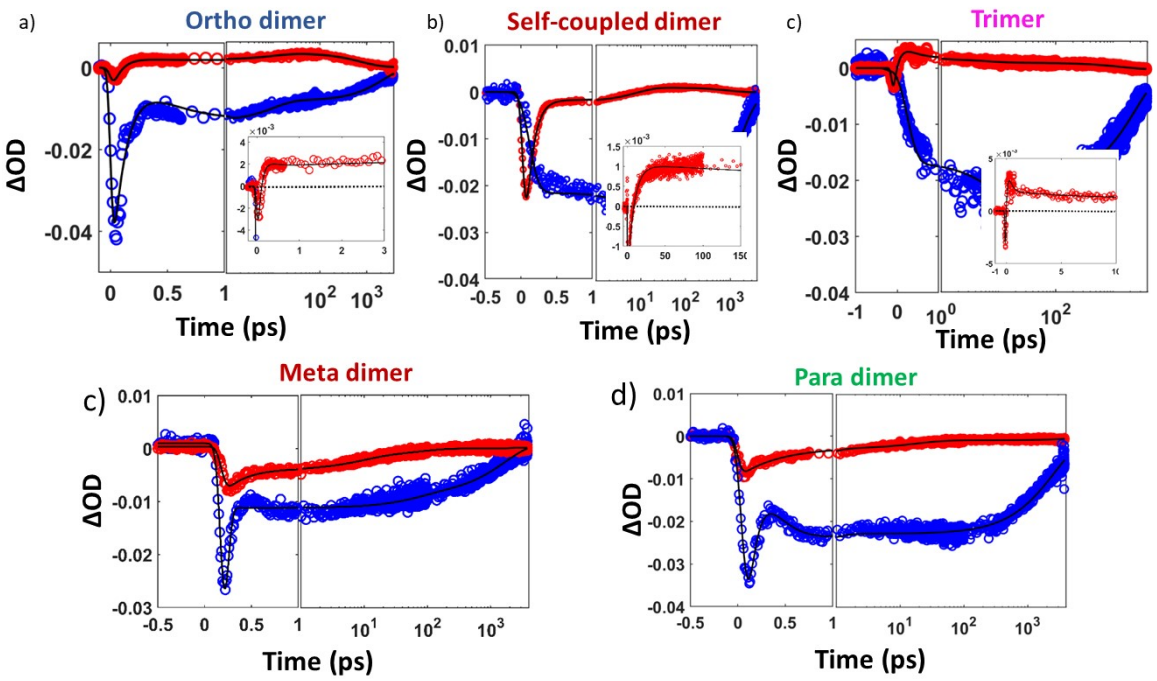

Fig. S53 Kinetics traces fitted with multi-exponential equation convoluted with Gaussian instrument response at 590 nm (radical cation absorption) for (a) *ortho*-PMI dimer, (b) self-coupled PMI dimer (c) 1,3,5-PMI trimer (d) *para*-PMI dimer and (e) *meta*-PMI dimer in Tol (raw data blue) and DMF (raw data red) along with black fit.

Table S8: Fit parameters for kinetic traces at of TA signal at position of radical cation (590 nm) for PMI-dimers in Tol and DMF.

λ (nm)	Comp	Solv.	α_1 (rise) (%)	τ_1 (ps)	α_2 (%)	τ_2 (ps)	α_3 (%)	τ_3 (ps)	α_4 (%)	τ_4 (ps)	α_5 (%)	τ_5 (ps)	R^2
Radical Cation (590 nm)	*ortho-*	Tol	47	0.2	-	-	51	0.18	5	10.2	1	2289	0.94
		DMF	54	0.12	-	-	0.1	11.12	45	0.12	0.9	760	0.94
	meta-	Tol	-	-	28	0.11	50	2.7	20	52.2	2	9011	0.92
		DMF	-	-	-	-	66	0.3	25	0.9	9	4554	0.95
	para-	Tol	34	0.01	-	-	64	0.01	1.9	69	0.1	1690	0.96
		DMF	-	-	54	0.2	28	9.1	14	76	4	8652	0.94
	SC	Tol	22	13.39	-	-	-	-	-	-	78	1513	0.96
		DMF	48	0.12	-	-	50	0.12	1	8.3	1	938	0.97
	Tri	Tol	27	10	-	-	-	-	19	100	54	2469	0.94
		DMF	56	0.7	-	-	41	0.2	2	6.1	1	1372	0.90

VII. Spectroscopic evidence of PMI radical species by chemical oxidation and spectroelectrochemistry methods:

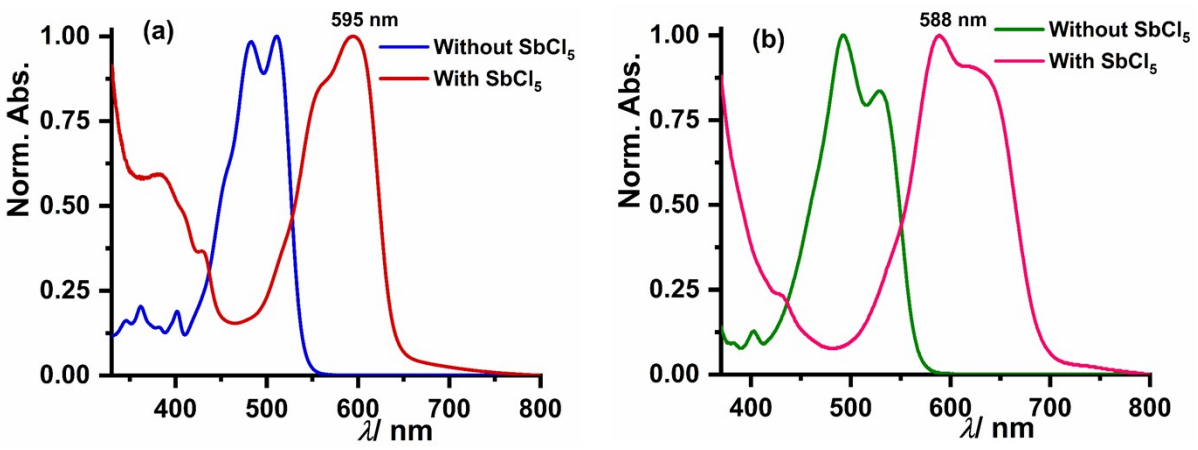

Fig. S54 Normalized UV-Vis. absorption spectra of PMI radical cation ($PMI^{\bullet+}$) corresponding to (a) reference PMI monomer (***o*-PMI-ac)** and (b) *ortho*-PMI dimer generated by treatment with $SbCl_5$ in dry DCM. The absorption band nearby 590 nm is corresponding to PMI radical cation ($PMI^{\bullet+}$) species.

Note: *The UV-Vis. titration of reference PMI or ortho-PMI dimer with highly oxidizing agent antimony pentafluoride ($SbCl_5$) was carried out to get evidence of origin of ~600 nm band in the transient absorption spectra for ortho-PMI dimer and self-coupled dimer. The addition of freshly prepared $SbCl_5$ in reference PMI or ortho-PMI dimer solution exhibited a drastic color change from yellowish-orange to blue which indicated formation of new species. Subsequently, the UV-Vis. absorption spectra were measured which showed emergence of distinct new band at 595 nm (for reference PMI), 588 nm and 623 nm (for ortho-PMI dimer). The peak positions exactly match with the peak observed in fs-TA spectra. This band at the red-shifted position than absorption maxima of both neutral derivatives signify formation of PMI radical cation species ($PMI^{\bullet+}$).*

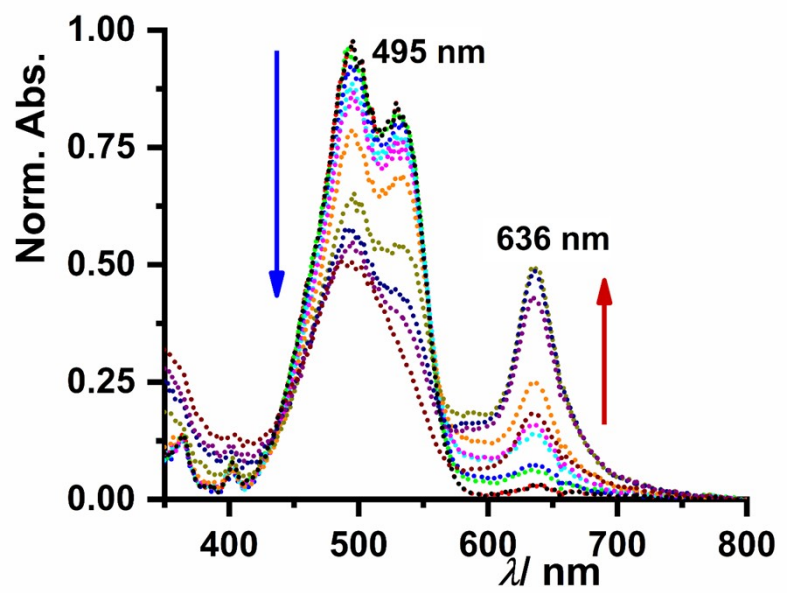

Fig. S55 Spectroelectrochemical data showing generation of $PMI^{\bullet-}$ for *ortho*-PMI dimer in dry DCM (Potential applied: -1.0 V).

Note: *The formation of PMI radical anion could not be detected by chemical reduction method using* $Co(Cp)_2$ *may be because cobaltocene is not strong enough to reduce. Also, it is reported in the literature that the reduction of PMI is comparatively difficult than PDI (*E_{Red} *= -0.96 V and -0.53 V for PMI and PDI respectively). To find the alternative way, we performed spectroelectrochemistry for ortho-PMI dimer in anhydrous DCM by applying the reduction potential at* E_{red} *= -1.0 V to monitor the evolution of* $PMI^{\bullet-}$*. The experiment revealed emergence of new sharp peak at 636 nm which can be assigned to absorption of π-π stacked PMI radical anion species. The absorption peak of π-π staked* $PMI^{\bullet-}$ *species generally appears nearby 640 nm as reported by Wasielewski and Hariharan groups.*[15, 16]

VIII. Electrochemical study:

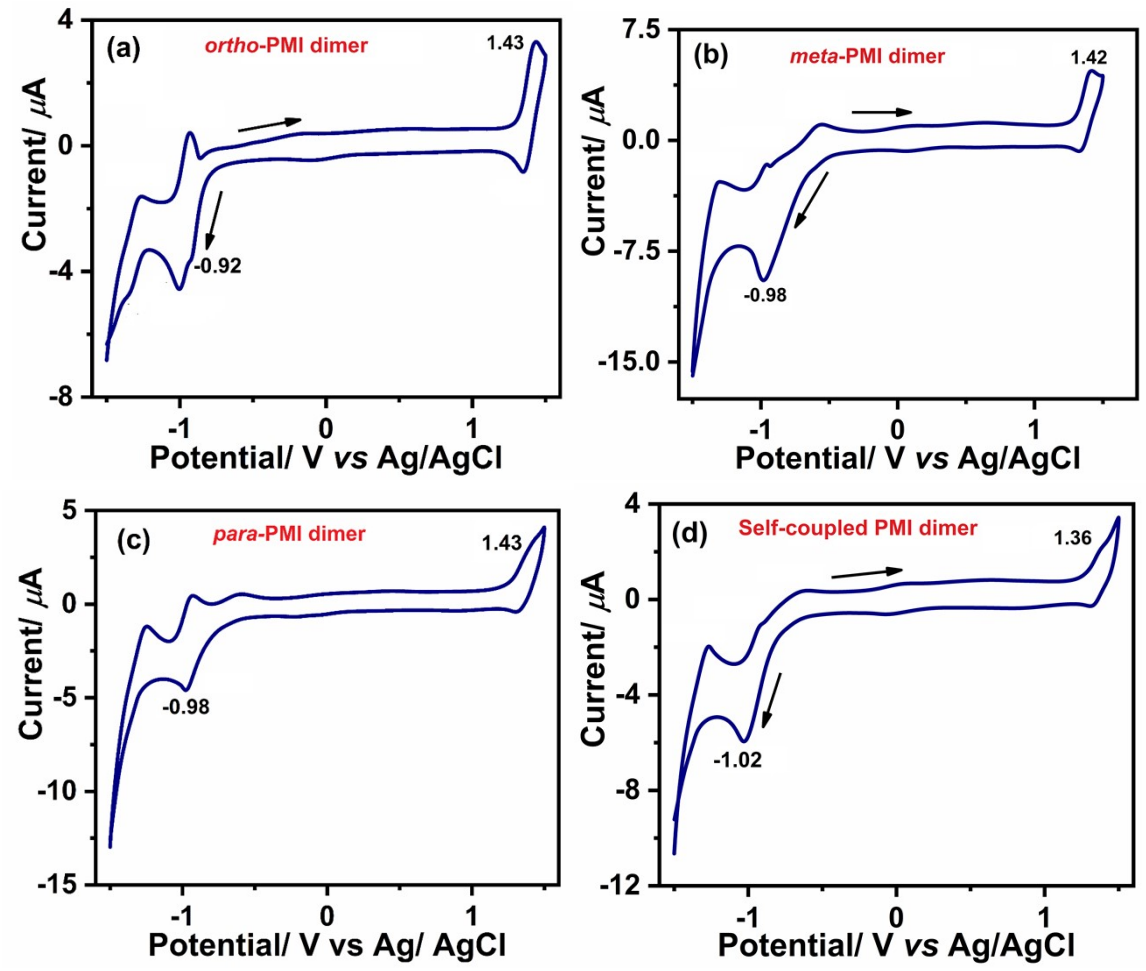

Fig. S56 Cyclic voltamogram of (a) *ortho*-PMI dimer (c) *meta*-PMI dimer (d) *para*-PMI dimer and (d) self-coupled PMI dimer measured in 0.1 M TBAP in anhydrous DCM using three-electrodes configuration.

Table S9. Charge-separation parameters for *meta*- and *para*-PMI dimers in three different solvents.

Compound	Solvent	E_{ox} (V)	E_{Red} (V)	$E_{0,0}$ (eV)	d_{DA} (Å)	r_D/ r_A (Å)	ΔG_{CS} (eV)
meta-PMI dimer	Tol	1.42	-0.98	2.30	14.90	4.75	+0.63
	$CHCl_3$	1.42	-0.98	2.28	14.90	4.75	+0.21
	DMF	1.42	-0.98	2.26	14.90	4.75	-0.14
para-PMI dimer	Tol	1.43	-0.98	2.26	18.54	4.75	+0.76
	$CHCl_3$	1.43	-0.98	2.24	18.54	4.75	+0.30
	DMF	1.43	-0.98	2.22	18.54	4.75	-0.09

IX. SB-CS scheme:

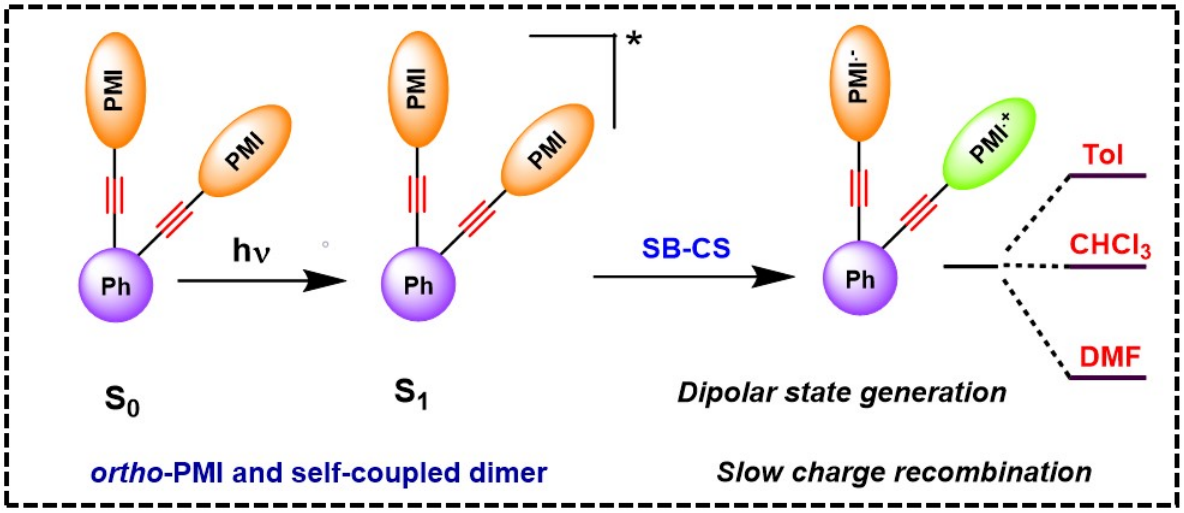

Fig. S57 Schematic illustration of SB-CS process investigated for two PMI dimers in this work.

X. Comparison of charge separation and charge recombination parameters:

Table S10. Summary of charge separation and charge recombination time constants (τ) of PDI/ PBI and PMI-based multichromophoric systems.

Sl. No.	System	Key factor for SB-CS	τ_{CS} (Solvent)	τ_{CR} (Solvent)	References
1	PMI-based regio-isomers with -Ph linker	dihedral twisting and solvent fluctuation	80.2 ps (DMF)	901 ps (DMF)	Present work
2	Cofacial and linear PDI dimers (***cof*-5PDI$_2$** and ***lin*-5PDI$_2$**)	Parallel π-stacked geometry in ***cof*-5PDI$_2$** facilitates CS in Toluene	170 fs (Toluene)	222 ps (Toluene)	*J. Am. Chem. Soc.* **2002**, *124*, 8530–8531
3	PDI molecular triangle (**PDI-Δ**)	Suppressing of excimer formation due to rigid triangle geometry	12.0 ps ($CHCl_3$)	1.12 ns ($CHCl_3$)	*J. Am. Chem. Soc.*, **2015**, *137*, 13236–13239
4	Cofacially-stacked PDI dimer (**PBI-CP**)	Excimer-mediated intra-molecular electron transfer	36.0 ps ($CHCl_3$)	1.1 ns ($CHCl_3$)	*J. Am. Chem. Soc.*, **2016**, *138*, 9029–9032
5	N-annulated PDI	Bridge-assisted tuning of	12.4 ps	1.94 ns	*J. Am. Chem.*

	dimers (***m*-BDNP** and ***p*-BDNP**)	electronic coupling in CS	(THF)	(THF)	*Soc.*, **2019**, *141*, 12789−12796
6	*Bay*-substituted PDI cyclophane	Solvent-modulated CT resonance enhancement in excimer state	23 ps (BZCN)	2.5 ns (BZCN)	*J. Phys. Chem. Lett.* **2019***, 10,* 1919–1927
7	Near-orthogonal PMI dimer (**PP**)	Orthogonal arrangement results weak-electronic coupling	2.8 ps (ACN)	1.2 ns (ACN)	*J. Phys. Chem. C*, **2020**, *124*, 237−245
8	Multibranched PDI tetramer (**PM-PDI$_4$**)	3D-geometry with crowded monomers enhances the through-space coupling	44.7 ps (DMF)	4.8 ns (DMF)	*J. Phys. Chem. Lett.*, **2020**, *11*, 10329−10339
9	Phenyl-bridged PDI dimers (***o*-PDI$_2$**, ***m*-PDI$_2$**, ***p*-PDI$_2$**)	Core distortion led by headland substitution for *ortho*-dimer	12.1 ps (DCM)	119 ns (DCM)	*J. Phys. Chem. A*, **2021**, *125*, 7633−7643
10	Null-exciton coupled PDI dimer (**Sp-PDI$_2$**)	Weak electronic coupling due to Greek cross (+) arrangement	0.627 ps (ACN)	1.66 ns (ACN)	*J. Am. Chem. Soc.*, **2021**, *143*, 13769−13781
11	Co-facial Green PBI cyclophane (**gPBI-CP**)	Formation of vibrationally coherent CT resonant excimer and breakdown of adiabaticity in excimer state	~1.0 ps (Tol)	Not determined	*J. Am. Chem. Soc.*, **2022**, *144*, 15539–15548
12	Null-type PDI dimer and trimer	Coherent vibronic coupling leading to mix FE and CT states	2.7 ps (THF)	0.224 ms (THF)	*Nat. Chem.*, **2022**, *14,* 786–793

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