



## NIR Dyes

# Electronic Modulation of Terrylene Diimides Leading to Core-Twisting, Tunable Emission and Intermolecular Interactions

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**Abstract:** Three new symmetrically *para*-phenylethynylenesubstituted terrylene diimide derivatives namely, **TDI-Ph**, **TDI-PhCN** and **TDI-PhNMe**<sub>2</sub> were synthesized to study the electronic effects on the structure and properties. The solid-state single-crystal structures for **TDI-Ph** and **TDI-PhCN** as well as for the precursor **TDI-Br**<sub>4</sub> are presented. The X-ray diffraction studies revealed twisting in the *bay*-area of terrylene core, which improved the solubility as well, despite of having some of the

#### Introduction

 $\pi$ -Conjugated organic molecules having robust structural framework and excellent photo and thermal stabilities are the need of the hour, for their potential utilities in modern electronic applications.<sup>[1]</sup> Rylene diimides (RDIs) are an important class of chromophores that possess sturdy polyaromatic molecular architecture together with solubility and stability. One way to augment the  $\pi$ -conjugation of these molecules is to fuse successive naphthalene units vertically along their peri-positions; this results in molecules having strong light absorption in near infra-red (NIR) region. Another strategy is to functionalize the *bay*-positions through annulations, thereby extending the  $\pi$ -conjugation in the horizontal direction of the molecule. In both the cases, the larger molecules possess very interesting properties, which might be useful for organic electronic applications. However, the higher homologues of RDIs are comparatively less explored due to their synthetic challenges and solubility limitations.<sup>[2]</sup>

Among larger RDIs, terrylene diimides (TDIs) have transpired as important dyes for single molecule spectroscopy studies, membrane labeling and enzyme tracking experiments because of their inherent higher absorption coefficients in the NIR region with high fluorescence quantum yields.<sup>[3–8]</sup> TDIs also exhibit high thermal and photochemical stabilities, which makes them compatible for use in organic field-effect transistors, photochromic switches, supramolecular self-assemblies, and organic solar cell applications.<sup>[9–16]</sup> The extended  $\pi$ -conjugation of TDIs show efficient charge transport properties.<sup>[17–19]</sup> TDIs generally suffer from poor solubility owing to a flat large  $\pi$ surface. The traditional way to make these dyes more soluble

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shortest intermolecular Br···Br and C-H···O interactions in **TDI-Br**<sub>4</sub>. All the compounds exhibited near infra-red absorption and emission except for **TDI-PhNMe**<sub>2</sub>; especially **TDI-PhNMe**<sub>2</sub> showed interesting broad absorption ranging from 300 to 970 nm. Further, the effects of electron-donating and accepting unit on electrochemical and optical properties have been investigated.

is by introducing tert-butyl-substituted phenoxy groups in the bay-region and diisopropylphenyl groups at the imide positions.<sup>[20,21]</sup> Several blue TDI derivatives were recently reported with metal catalyzed hetero-coupling reactions such as Suzuki, Stille, and Sonogashira coupling with the 1,6,9,14-tetrabromo TDI building block.<sup>[22-24]</sup> The palladium-catalyzed benzannulation of tetrabromo TDI with o-trimethylsilyl phenyl triflate resulted in core enlarged atropisomers of TDI.<sup>[22]</sup> The Suzuki or Stille coupled TDI derivatives were subsequently transformed to core expanded molecules using metal oxidants. For instance, tetra-ethynylene-1-dodecyne substituted TDI was in-situ converted to core annulated derivative using DBU.<sup>[23]</sup> Owing to the steric encumbrance effect of substituents, these derivatives have been predicted to have a non-planar conjugated core.<sup>[22,24]</sup> Hence, there is a need to deduce the structure-property relationship using diverse examples to exploit the optical and electrochemical properties of functionalized TDI derivatives. Further, there is no solid state structural proof available for bay-functionalized TDI derivative till date, even though there are a few striking solid-state structural proofs for TDI and orthosubstituted TDI exist.<sup>[18]</sup> In our previous research work, we reported the synthesis of different unsymmetrical perylene diimide (PDI) derivatives and their solid-state structure-property relationship.<sup>[25–29]</sup> Therefore, we set out to explore TDIs, which are higher homologous of PDIs, with higher degrees of freedom to deviate from planarity. We were particularly interested in the symmetrical functionalization of TDI bay-regions (1,6,9,14-positions) via ethynylene bridge using para-phenyl-substituted derivatives by Sonogashira coupling reactions, which may impart twisting in the terrylene core due to steric crowd and hence will improve the solubility as well.

We present, herein, the design and synthesis of three new ethynylphenyl flanked TDI derivatives. Further, the photophysical and electrochemical properties were investigated to understand the effect of electron withdrawing (-CN) and donating (-NMe<sub>2</sub>) groups substituted on the *para*-position of the aryl arms.

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### **Results and Discussion**

The synthetic route utilized for obtaining TDI-Ph, TDI-PhCN and TDI-PhNMe<sub>2</sub> is depicted in Scheme 1. The precursor molecules PMI and NMI were synthesized as per modified reported methods. The parent TDI molecule and 1,6,9,14-tetrabromo TDI (TDI-Br<sub>4</sub>) derivative were prepared according to the procedures established by Müllen et al.[21,30] The target molecules were synthesized by cross-coupling between respective alkynes and TDI-Br<sub>4</sub> under Sonogashira conditions in presence of [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and Cul. In all these cases of TDI-Ph, TDI-PhCN, and TDI-PhNMe<sub>2</sub>, the reactions proceeded smoothly and the products were obtained in 70-80 % isolated yields. The <sup>1</sup>H NMR and <sup>1</sup>H-<sup>1</sup>H correlation spectroscopy studies confirmed the symmetrical substitution at the bay-area. The High-Resolution-Atmospheric Pressure Chemical Ionization (HR-APCI) mass spectra confirmed the formation of these molecules. The complete spectroscopic characterization including NMR and high resolution mass spectra (HRMS) for all the compounds are provided

in ESI. The compounds **TDI-Ph**, **TDI-PhCN** show good solubility in common organic solvents such as chloroform, dichloromethane, toluene, and tetrahydrofuran. Whereas **TDI-PhNMe<sub>2</sub>** shows good solubility in solvents such as chloroform, dichloromethane and poor solubility in toluene, and tetrahydrofuran. The thermogravimetric analysis (TGA) under nitrogen indicates that all three derivatives exhibit high thermal stability and show decomposition temperature above 400 °C for all molecules (Figure S40).

In case of *bay*-substitution of PDIs, it has been seen that the molecules tend to lose their planarity.<sup>[25,29]</sup> To corroborate the same for TDI, due to a longer  $\pi$ -conjugated core, structural characterization was necessary. Even though there are single-crystal X-ray diffraction structures reported for a TDI and an *or*-tho-substituted TDI by Wasielewski and co-workers,<sup>[18]</sup> there has been no structural proof available yet for *bay*-substituted TDIs. Hence, it becomes very crucial and important to investigate the solid-state structure to develop the structure-property relationship. Efforts were directed towards crystallizing of the prepared



Scheme 1. Synthetic route to symmetrically functionalized core-twisted TDI dyes.







Figure 1. The single-crystal X-ray diffraction structures of (A) **TDI-Br**<sub>4</sub> (B) **TDI-Ph** (C) Br-Br and (D) C-H-O interaction in **TDI-Br**<sub>4</sub> (substituents on the imidepositions are omitted for clarity).

molecules. After several trials, suitable single crystals were obtained by solvent vapor diffusion of hexane into the toluene solution of TDI-Br<sub>4</sub>, tetrahydrofuran solution of TDI-Ph, and dichloromethane solution of TDI-PhCN, respectively. In the case of TDI-PhNMe<sub>2</sub> several attempts with various solvents were made but X-ray quality crystals could not obtained. In case of TDI-PhCN, there are a few disordered dichloromethane solvent molecules seen. The diffraction data for TDI-PhCN (CCDC No. 1890583) was weak, probably due to the longer side groups and structural disorders of the solvent molecules, and therefore the data has not been used to discuss bond angles and distances but used only as a structural proof (Figure S29). A close examination of the crystal structures reveal a non-planar framework for the aromatic terrylene core for all the molecules as depicted in Figure 1. The central naphthalene units in the terrylene core deviated from coplanarity due to steric crowd at the bay-region. For **TDI-Br**<sub>4</sub> (CCDC No. 1890579), C<sub>16</sub>C<sub>17</sub>C<sub>18</sub>C<sub>1</sub> and C<sub>14</sub>C<sub>25</sub>C<sub>26</sub>C<sub>15</sub> dihedral angles are 21.36° and 25.69°, respectively. The bromine atoms are deviated by 13.65° and 5.54° torsion angles for C17C18C1Br1 and C26C25C14Br2 planes, respectively. In TDI-Ph (CCDC No. 1890581), the naphthalene units are twisted by 9.34° and 18.03°, respectively for C<sub>1</sub>C<sub>18</sub>C<sub>22</sub>C<sub>8</sub> and C<sub>6</sub>C<sub>20</sub>C<sub>21</sub>C<sub>7</sub> dihedral planes. The ORTEP diagrams of all the molecules with atom numbering have been provided in ESI (Table S2).

The structure of **TDI-PhNMe<sub>2</sub>** has been optimized using DFT calculations<sup>[31]</sup> and shown in ESI (Figure S30 and S31). The adja-

cent naphthalene units in **TDI-PhNMe<sub>2</sub>** are deviated from coplanarity by 17.91°, 18.19°, 18.15°, and 18.34°, respectively for the  $C_1C_6C_{23}C_{27}$ ,  $C_2C_3C_{11}C_{14}$ ,  $C_8C_7C_{13}C_{20}$ , and  $C_9C_{10}C_{21}C_{28}$  dihedral angles as observed from the optimized structure. In case of *bay*-monobromo-PDI too, the bromine atom was protruding above the PDI plane but after the functionalization the core was found to be planar.<sup>[25]</sup> Therefore, it was expected that in TDIs as well, the same effect may prevail. However, in the present case, the four substituents seem to force the core to deviate from planarity due to the larger steric hindrance.

A striking feature in the solid-state structure of TDI-Br<sub>4</sub> is the extensive network of strong non-covalent interactions. Intermolecular bromine-bromine interactions usually are difficult to find and only a few examples are known with short contacts between the bromines.<sup>[32]</sup> Surprisingly, in case of TDI-Br<sub>4</sub>, a bay-substituted bromine atom is found to interact with its counterpart from the nearest neighbour with metric parameters for C-Br-Br with a distance of 3.3075(5) Å and an angle of 152.1(1)° (Figure 1C). This is one of the shortest bromine-bromine contacts, the shortest reported one having a distance of 3.2 Å, much shorter than the sum of van der Waals' radii of 3.7 Å, demonstrating the stabilizing nature of the interaction.<sup>[33]</sup> Moreover, two complimentary short C-H--O interactions (2.285 Å & 168.5°) involving ortho-hydrogens and the oxygens from imido-groups of two neighbouring molecules further stabilizing the solid state packing as shown in Figure 1D.



To identify the effect of alkynyl phenyl substituents on the electronic nature of the newly synthesized molecules, UV/Vis-NIR absorption spectra in diluted chloroform solution were measured and shown in Figure 2. TDI shows strong absorption from 500 to 700 nm with three typical TDI core vibronic features with maxima at 662 nm and a molar absorption coefficient of  $1.24 \times 10^5 \text{ m}^{-1} \text{ cm}^{-1}$ . The newly synthesized molecules show bathochromic shifts as compared to TDI due to the extension of  $\pi$ -conjugation by four alkynylphenyl groups. Compounds TDI-Ph and TDI-PhCN show a red-shift of about 79 and 75 nm relative to parent **TDI**, resulting in an absorption maxima at 741 and 737 nm with molar absorption coefficients of 8.7 and  $7.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. Both the compounds show vibronic fine structures in the 600 to 800 nm wavelength region corresponding to strongly allowed S<sub>0</sub>-S<sub>1</sub> transition of the **TDI** core, by analogy with PDIs.<sup>[34]</sup> Compound **TDI-PhNMe**<sub>2</sub> displays an interesting absorption pattern, as compared to other two derivatives. It exhibits a broad absorption ranging from 300 to 970 nm with a maximum absorption at 858 nm  $(\varepsilon = 4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$  in the NIR region with the loss of vibronic features. The broad and structureless band with a maximum at 858 nm is assigned to a charge transfer (CT) transition from HOMO of N,N-dimethylaminophenyl moiety to the LUMO of TDI core. The broadening of band between 600 to 800 nm can be assigned to HOMO to LUMO transition of the TDI core, overlapping with the CT band. All the new molecules display intense absorption in the 300 to 500 nm region and can be attributed to  $S_0-S_2$  transition.<sup>[3,35]</sup> Although the three new derivatives show red-shift in absorption spectra by the introduction of alkynylphenyl fragments, the molar absorption coefficients were reduced significantly. This is attributed to the twisting in the aromatic terrylene core due to bulky alkynyl phenyl groups at the bay-area, and hence removing the coplanarity at the TDI core.<sup>[16]</sup> The optical data have been summarized in Table 1.



Figure 2. Absorption spectra of **TDI**, **TDI-Ph**, **TDI-PhCN** and **TDI-PhNMe**<sub>2</sub> in chloroform ( $10^{-6}$  M) solution.

| Table 1. C | Optical and | electrochemical | data of | <sup>:</sup> all | compounds |
|------------|-------------|-----------------|---------|------------------|-----------|
|------------|-------------|-----------------|---------|------------------|-----------|

| Compound               | λ <sub>abs, max</sub><br>[nm] | ε<br>[M <sup>-1</sup> cm <sup>-1</sup> ] | λ <sub>em, max</sub><br>[nm] | Ф<br>[%] | E <sub>red</sub><br>[V] | E <sub>ox</sub><br>[V] |
|------------------------|-------------------------------|--|------------------------------|----------|-------------------------|------------------------|
| TDI                    | 662                           | 124000                                   | 667                          | 90*      | -0.62                   | 1.15                   |
| TDI-Ph                 | 741                           | 87000                                    | 758                          | 16       | -0.49                   | 1.16                   |
| TDI-PhCN               | 737                           | 70000                                    | 754                          | 22       | -0.35, -0.45            | 1.26                   |
| TDI-PhNMe <sub>2</sub> | 858                           | 40000                                    | -                            | -        | -0.58                   | 0.87, 1.24             |



To obtain insights into the role of substituents in determining the other optical properties of these symmetrically substituted systems, emission studies were performed from chloroform solutions. Compounds TDI, TDI-Ph and TDI-PhCN were strongly fluorescent but TDI-PhNMe2 was non-fluorescent in chloroform solution. Compounds TDI-Ph and TDI-PhCN showed broad, structure less emission spectra with maximum emission at 758 and 754 nm, respectively as shown in Figure 3. The broadening of emission bands may be attributed to the twisting in the aromatic terrylene core. The fluorescence guantum yields obtained were 16 and 22 % for TDI-Ph and TDI-**PhCN**, respectively with respect to parent **TDI** ( $\Phi = 90$  %) as reference.<sup>[7,8]</sup> The emission from TDI-PhNMe<sub>2</sub> was guenched, further supporting the CT transition from dimethylaminophenyl group to the **TDI** core. The fluorescence data has been given in Table 1.



Figure 3. Normalized fluorescence spectra of **TDI**, **TDI-Ph** and **TDI-PhCN** in chloroform ( $10^{-6}$  M) solution with excitation at 550 nm.

Further, the solvent dependent fluorescence studies in various solvents such as toluene, THF, DCM, DMF, DMSO and methanol for **TDI**, **TDI-Ph** and **TDI-PhCN** were conducted and the spectra are provided in ESI (Figure S36–S38). The quenching in fluorescence was observed upon increasing solvent polarity perhaps due to aggregation of the molecules. The solvent dependent absorption of **TDI-PhNMe**<sub>2</sub> resulted in decreased molar absorptivity (Figure S35) of the CT band at 859 nm and 23 nm red-shift in the band hinting that the CT state is being stabilized as solvent polarity increases.

To further confirm the CT characteristics in **TDI-PhNMe**<sub>2</sub>, a protonation study of electron-rich dimethylaminophenyl moiety using trifluoroacetic acid (TFA) was conducted in chloroform solution. Upon protonation, the broad absorption band in the NIR region diminished and a new absorption spectrum with fine vibronic structure similar to **TDI-Ph** appeared as shown in Figure 4. The newly emerged spectrum exhibited absorption ranging from 300 to 800 nm with maxima at 737 nm. Further, the originally quenched fluorescence was regained after protonation. The emission spectrum showed maxima at 756 nm with a shoulder at 676 nm. Hence, the intramolecular CT interactions are suppressed as the electron-rich dimethylamino unit gets protonated.

The redox properties of the synthesized molecules were investigated by cyclic voltammetry studies to elucidate the effect







Figure 4. Absorption (solid line) and emission (dash line) spectrum of **TDI-PhNMe<sub>2</sub>** before and after protonation using TFA.

of electron-donating and accepting units. The electrochemical measurements were done in dichloromethane containing tetrabutylammonium hexafluorophosphate as a supporting electrolyte with respect to saturated calomel electrode (SCE) at a scan rate of 100 mV/s. The cyclic voltammograms are shown in Figure 5 and the redox potentials are listed in Table 1. TDI shows one reversible reduction and one reversible oxidation wave at -0.62 and 1.15 V, respectively vs SCE. TDI-Ph also exhibits one reversible reduction and one reversible oxidation wave, respectively at -0.49 and 1.16 V. However, TDI-PhCN shows two reversible reduction waves at -0.35 and 0.45 V, and one reversible oxidation wave at 1.26 V. Compared to TDI and TDI-Ph, TDI-PhCN is easier to reduce, thus demonstrating its strong acceptor ability. Compound TDI-PhNMe<sub>2</sub> exhibits one reversible reduction wave at -0.58 V and two oxidation potential waves at 0.87 and 1.24 V. The appearance of oxidation potential at 0.87 V in this molecule hints toward the strong electron-donating ability of the dimethylaminophenyl moiety.



Figure 5. Cyclic voltammogram of compounds in dichloromethane at 100 mV/ s scan rate with respect to SCE with TBAP as the supporting electrolyte.

To visualize the electron delocalization in frontier molecular orbitals DFT calculations were performed at the B3LYP/6-31g (d,p) level using *Gaussian 09 suite* of programs.<sup>[31]</sup> The HOMO and LUMO are delocalized over the whole terrylene core in **TDI** with a node passing through the N,N-axis. The electron density in **TDI-Ph** and **TDI-PhCN** were delocalized over TDI core with contribution from ethylene linker in both HOMO and LUMO. However, for **TDI-PhNMe**<sub>2</sub>, the HOMO was delocalized over whole molecule including the electron-rich dimethylamino moiety, and LUMO predominantly over the TDI core. The frontier molecular orbitals with energy levels have been shown in Figure 6. Hence, the broad absorption band between 600 to 970 nm can be assigned for extension of conjugation and CT transition, which also has contribution from HOMO and LUMO.



Figure 6. DFT computed frontier molecular orbital energy levels of compounds.

#### Conclusions

In summary, we present here the synthesis of three new symmetrical ethynylphenyl-substituted TDI derivatives. For the first time for any bay-substituted TDI derivative, solid-state structural proof for the building block **TDI-Br**<sub>4</sub> and two newly prepared molecules TDI-Ph and TDI-PhCN have been provided. The single-crystal X-ray structures revealed twisting of the terrylene cores due to the steric encumbrance at the bay-regions. The brominated TDI derivative showed one of the shortest Br---Br interactions reported to date along with strong C-H--O interactions as well to stabilize solid state packing. The optimized geometry of TDI-PhNMe<sub>2</sub> shows a highly twisted structure for this molecule. All the molecules displayed panchromatic absorption ranging from 300 to 800 nm. The interesting absorption behaviour of TDI-PhNMe<sub>2</sub> due to CT transition was observed with a broad absorption ranging from 300 to 970 nm. The CT characteristic of this molecule was probed by protonation of electron-rich dimethylamino unit, which resulted in bathochromically shifted absorption band along with emission. The compounds showed NIR fluorescence emission from 560 to 800 nm except for TDI-PhNMe2. The electrochemical studies revealed drastic change in frontier orbital energy levels due to electron-donating and withdrawing units on phenyl ring. Owing to wide and strong absorption in NIR region with suitable electronic energy levels makes these molecules suitable material for the fabrication of light weight organic solar cells. Further studies to exploit these molecules towards these applications are underway in our laboratory.



## **Experimental Section**

Materials and methods: All reactions were carried out under argon atmosphere wherever required. Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Samples synthesized were purified by silica gel (100-200 mesh) column chromatography followed by recrystallization. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 500 MHz spectrometer in CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> solvents. The chemical shift values have been referenced to the residual solvent signals. HRMS measurements were recorded on a microTOF-QII high resolution mass spectrometer from Bruker Daltonics coupled to a Waters Acquity UPLC system. Steady-state absorption measurements were done on carry 5000 UV/Vis/NIR spectrophotometer. Steady-state fluorescence emission measurements were done on a Horiba Jobin Yvon fluorolog 3-111. Quartz cell with optical path length of 10 mm was used for all measurements. Cyclic voltammetric measurements were carried out using CH potentiostat from CHI Instruments. CV experiments were done under continuous argon flow and a conventional three-electrode electrochemical cell was used. A glassy carbon working, a platinum wire counter and saturated calomel electrode (SCE) reference electrodes were used. All the measurements were done in dry dichloromethane solution with 0.1 M Tetrabutylammonium hexafluorophosphate (TBAP) as supporting electrolyte. All the spectra were recorded at a scan rate of 100 mV/s. Single crystal X-ray diffraction measurements were done on a Bruker Apex diffractometer with a CCD detector with Mo- $K_{\alpha}$  radiation. DFT Calculations were performed using Gaussian 09 software suite. The TGA measurements were done on PerkinElmer TGA 4000 instrument at scan rate of 10 °C/min under nitrogen purge (20 mL/min).

**Synthesis of NMI**: The compound was prepared as per the reported literature procedure.<sup>[36]</sup> To a solution of NMA (5.05 mmol, 1.0 g) in glacial acetic acid (20 mL), 2,6-diisopropylaniline (6.06 mmol, 1.2 mL) was added and heated at 110 °C for 5 hours with continuous stirring. After that the reaction mixture was cooled to room temperature followed by filtration and washed with distilled water and dried. Further purification was done using silica-gel column chromatography in ethyl acetate/hexane solvent mixture (3:7) to afford **NMI** as white solid (1.62 g, 89 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 8.70 (d, *J* = 7.2 Hz, 2H), 8.33 (d, *J* = 8.4 Hz, 2H), 7.84 (t, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.78 (m, 2H), 1.18 (d, *J* = 6.9 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 164.21, 145.68, 134.19, 131.85, 131.74, 130.86, 129.50, 128.83, 127.04, 124.02, 122.78, 29.13, 23.99. HRMS (ESI) (*m/z*): [M + Na]<sup>+</sup> calculated for C<sub>24</sub>H<sub>23</sub>NO<sub>2</sub>Na, 380.1621; found 380.1647.

Synthesis of PMI: This compound was synthesized using a literature procedure.<sup>[37]</sup> A solution of PDA (9.34 mmol, 3.66 g), 2,6-diisopropylaniline (5.12 mmol, 0.91 g), zinc acetate dihydrate (7.19 mmol, 1.32 g), and imidazole (275 mmol, 18.70 g) in 8 mL of water was heated at 190 °C for 23 hours in a sealed tube. Then the reaction mixture was extracted using chloroform and filtered through celite. The filtrate was then washed with 2M HCl solution and washed with water. The organic layer was collected over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Then crude mixture was purified by silica-gel column chromatography using chloroform/ hexane eluent (3:2) to produce the desired compound PMI as red solid (1.26 g, 28 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 8.66 (d, J = 8.0 Hz, 2H), 8.45 (mixed doublets, 4H), 7.92 (d, J = 7.9 Hz, 2H), 7.65 (t, J = 7.8 Hz, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.37 (d, J = 7.8 Hz, 2H), 2.85–2.77 (m, 2H), 1.22 (d, J = 6.9 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 164.00, 145.71, 137.53, 134.31, 132.01, 131.07, 130.96, 130.56, 129.44, 129.21, 127.99, 127.07,



124.02, 123.84, 121.00, 120.20, 29.16, 24.03. HRMS (APCI) (m/z): [M + H]<sup>+</sup> calculated for C<sub>34</sub>H<sub>27</sub>NO<sub>2</sub>H, 482.2115; found 482.2141.

Synthesis of TDI: The precursor was synthesized using the procedure reported by Müllen and co-workers.<sup>[21]</sup> In a dry Schlenk tube PMI (2.08 mmol, 1 g), NMI (8.32 mmol, 2.96 g) and sodium tertbutoxide (41.58 mmol, 3.99 g) were added. Then the degassed solution of 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) (41.58 mmol, 5.13 mL) and diglyme (5 mL) was injected into the tube under argon atmosphere. The mixture was vigorously stirred at 130 °C for 3 hours. After cooling to room temperature, the mixture was poured into water to give a precipitate. The resultant precipitate was filtered through suction and the dark crude compound was washed with ethanol until the colour of the filtrate became light red. Further, recrystallisation was done using chloroform/ethanol to give **TDI** as blue solid (620 mg, 36 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 8.69 (d, J = 8.0 Hz, 4H), 8.64 (s, 4H), 8.57 (d, J = 8.1 Hz, 4H), 7.43 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 4H), 2.71 (m, 4H), 1.13 (d, J = 6.8 Hz, 24H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 163.77, 145.70, 136.14, 132.06, 131.19, 129.59, 128.79, 124.61, 124.09, 121.92, 121.59, 29.71, 29.21, 24.03. HRMS (APCI) (m/z): [M + H]+ calculated for C<sub>58</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>H, 835.3530; found 835.3542.

Synthesis of TDI-Br<sub>4</sub>: Bromination of TDI was performed as per the procedure reported by Müllen et al.[30] The mixture of TDI (0.12 mmol, 100 g) and bromine (excess) in chloroform was stirred at 50 °C for 12 hours. After which the excess bromine was quenched with saturated Na<sub>2</sub>SO<sub>3</sub> solution. The organic layer was separated, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude mixture was subjected to silica-gel column chromatography and the pure tetrabromo-TDI derivative was isolated by dichloromethane/hexane solvent mixture (2:3) as blue solid (112 g, 81 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm) 9.48 (s, 4H), 8.94 (s, 4H), 7.45 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 4H), 2.72-2.62 (m, 4H), 1.13 (d, J = 6.8 Hz, 24H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm) 162.44, 145.63, 138.50, 137.19, 134.39, 129.30, 127.71, 124.24, 121.55, 120.48, 29.30, 24.04. HRMS (APCI) (m/z):  $[M + H]^+$  calculated for  $C_{58}H_{42}Br_4N_2O_4H$ , 1146.9951; found 1146.9919.

Synthesis of TDI-Ph: In a dry and argon flushed Schlenk tube Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.0044 mmol, 3 mg), Cul (catalytic) and TDI-Br<sub>4</sub> (0.0435 mmol, 50 mg) were added. Then dry diisopropylamine (5 mL) and dry THF (5 mL) was injected into this tube and the resulting mixture was degassed with argon for 15 minutes. Thereafter phenylacetylene (0.2174 mmol, 24 µL) was added and stirred the reaction mixture at 70 °C for 8 hours. After the completion of reaction, the mixture was concentrated under reduced pressure and purified using silica-gel column chromatography. The pure desired compound was isolated in dichloromethane/hexane eluent (4:1) as green solid (43 mg, 81 %). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm) 10.27 (s, 4H), 8.92 (s, 4H), 7.57 (d, J = 7.5 Hz, 8H), 7.53 (t, J = 7.9 Hz, 2H), 7.38 (d, J = 7.9 Hz, 4H), 7.34 (t, J = 7.5 Hz, 4H), 7.22 (t, J = 7.7 Hz, 8H), 2.80 (m, 4H), 1.18 (d, J = 6.8 Hz, 24H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta$  (ppm) 163.31, 146.21, 138.52, 135.66, 131.77, 131.12, 130.84, 129.64, 129.37, 128.76, 128.57, 128.07, 127.99, 127.61, 124.22, 122.40, 120.89, 119.50, 98.29, 91.44, 29.31, 23.86. HRMS (APCI) (*m/z*): [M + H]<sup>+</sup> calculated for C<sub>90</sub>H<sub>62</sub>N<sub>2</sub>O<sub>4</sub>H, 1235.4782; found 1235.4785.

**Synthesis of TDI-PhCN**: This compound was synthesized using the above procedure with ethynylbenzonitrile (0.2174 mmol, 28 mg), and obtained a green solid (42 mg, 74 %). <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ , 298 K)  $\delta$  (ppm) 10.12 (s, 4H), 9.05 (s, 4H), 7.64 (d, J = 8.2 Hz, 8H), 7.54 (mixed doublet & triplet, 10H), 7.38 (d, J = 7.9 Hz, 8H), 2.77 (m, 4H), 1.17 (d, J = 6.8 Hz, 24H). <sup>13</sup>C NMR (126 MHz,  $CD_2Cl_2$ ,



298 K)  $\delta$  (ppm) 163.07, 146.04, 138.45, 136.29, 132.29, 132.10, 130.84, 130.78, 129.73, 128.69, 128.55, 127.88, 127.79, 126.89, 124.23, 121.24, 118.82, 117.94, 112.66, 95.19, 94.88, 29.24, 23.73. HRMS (APCI) (*m/z*): [M]<sup>+</sup> calculated for C<sub>94</sub>H<sub>58</sub>N<sub>6</sub>O<sub>4</sub>, 1335.4546; found 1335.4528.

**Synthesis of TDI-PhNMe<sub>2</sub>**: This compound was synthesized using the above procedure with N,N-dimethyethylenebenzene (0.2174 mmol, 32 mg), and obtained a dark green solid (43 mg, 71 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 10.32 (s, 4H), 8.91 (s, 4H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 8H), 7.31 (d, *J* = 7.9 Hz, 4H), 6.44 (d, *J* = 9.0 Hz, 8H), 2.89 (s, 24H), 2.76 (m, 4H), 1.16 (d, *J* = 6.8 Hz, 24H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 163.49, 145.79, 138.01, 134.89, 133.33, 130.82, 129.66, 128.80, 128.12, 127.12, 124.13, 120.51, 29.27, 24.06. HRMS (APCI) (*m*/*z*): [M + H]<sup>+</sup> calculated for C<sub>98</sub>H<sub>82</sub>N<sub>6</sub>O<sub>4</sub>H, 1407.6470; found 1407.6443.

CCDC 1890583 (for **TDI-PhCN**), 1890579 (for **TDI-Br**<sub>4</sub>), and 1890581 (for **TDI-Ph**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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