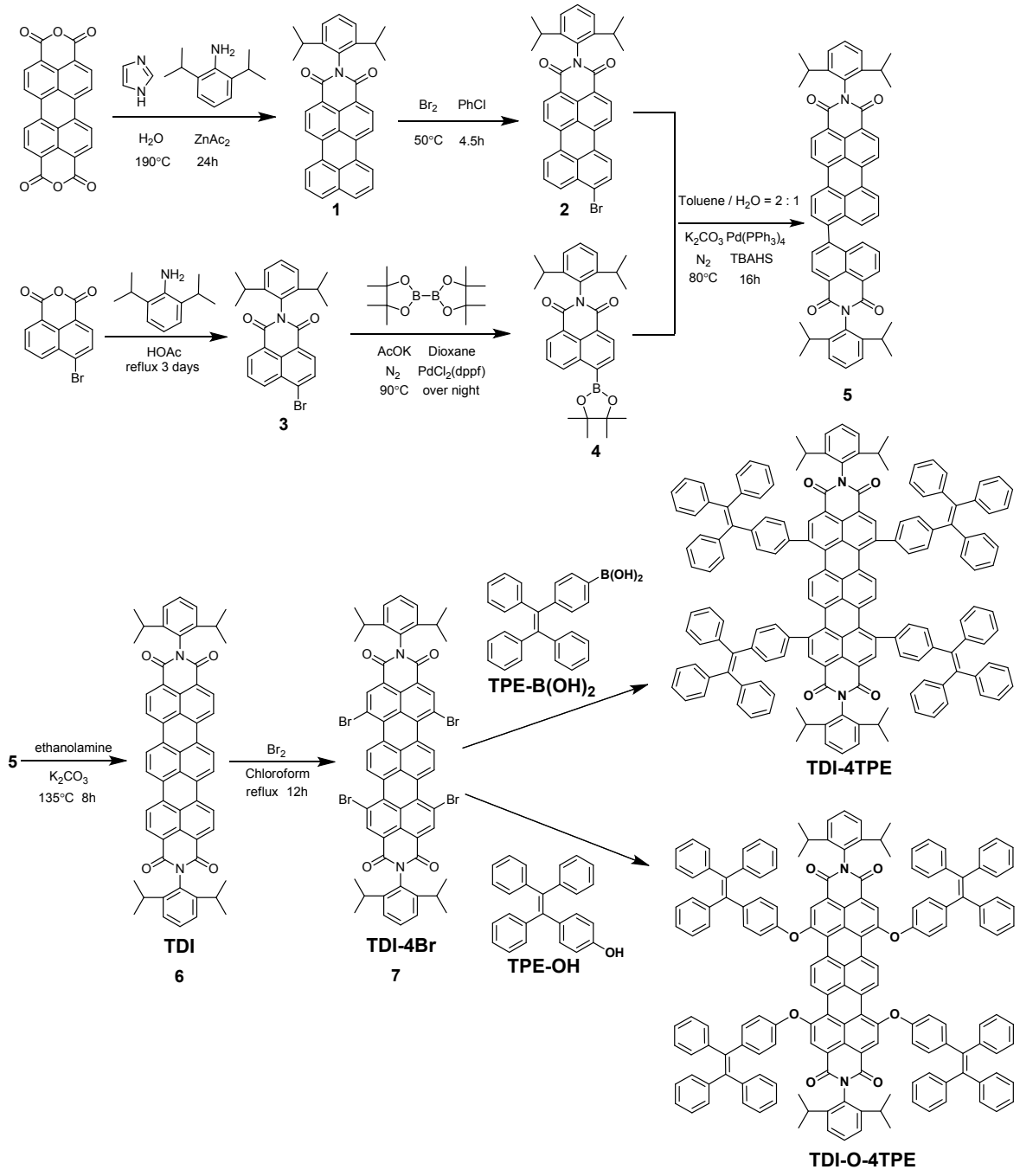
ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis and Aggregation-Induced Near-Infrared Emission of Terrylenediimide-Tetraphenylethene Dyads

Nuo-Hua Xie,[a] Chong Li, *[a] Jun-Xia Liu,[a] Wen-Liang Gong,[a] Ben Zhong Tang,*[b] Guigen Li,*[c] and Ming-Qiang Zhu*[a,c]

CONTENTS

1. EXPERIMENTAL.



Scheme 1 Synthesis routes to TDI-4TPE and TDI-O-4TPE conjugates.

(a) INSTRUMENTATION.

All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were purchased from Energy, Aladdin, alfa aesar, J&K and Sinopharm Chemical Reagent Co. Ltd. All reactions were carried out under a dry nitrogen atmosphere and the temperatures were measured externally. Toluene, dioxane and tetrahydrofuran (THF) were dried using sodium wire and benzophenone as the indicator. Other solvents were dried over CaH_2 with stirring overnight followed by distillation under reduced pressure. Reported yields are isolated yields. Purification of all final products was accomplished by gravity column chromatography, using silica gel. For qualitative purity tests of all intermediates and final products, a single spot (visualized using UV-light at 254 nm and 365 nm) was obtained on thin film chromatography plate. The purity of TDI-4TPE and TDI-O-4TPE were obtained on a Waters Breeze 2 HPLC with UV detector (254 nm) using a 5 μm CN column and eluting with DCM/hexane binary mixed solvent), and was further checked by elemental analysis (Elementar Vario Micro-cube). The UV-Vis absorption and photoluminescence emission of the compounds were recorded on Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600) and Edinburgh instruments (FLS 920 spectrometers), respectively. For the measurement of the fluorescence time profiles, time-correlated single-photon counting method using a picosecond pulsed light emitting diode (Edinburgh Instruments Ltd., EPLED-340, 339.6 nm, Pulse width = 602.3 ps, the Instrument response function is measured 104 ps) with 10MHz repetition rate was employed. The NMR spectra were recorded using a 600M Bruker AscendTM 600MHZ in $CDCl_3$ or CD_2Cl_2 and an internal standard of tetramethylsilane was used. The relative fluorescence quantum yields were estimated using N,N'-di(2,6-diisopropylphenyl)terrylene-3,4:11,12-tetracarboxdiimides in chloroform as standard material. The Mass spectra were recorded using an Agilent 1100 LC/MSD Trap. MALDI TOF mass spectra were recorded with a MALDI-TOF-TOF (Bruker ultrafleXtreme). Polystyrene (PS) film of TDI, TDI-4Br, TDI-4TPE, TDI-O-4TPE were prepared by spin coating of chloroform solution containing PS polymer (100mg/mL) and dyes (0.1 mg/mL, 0.5 mg/mL, 1 mg/mL, respectively) at 400 rpm for 2s and then 2000rpm for 40s onto clean quartz plates.

(b) SYNTHESIS PROCEDURES.

N-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide **(1),**[1]
N-(2,6-diisopropylphen-yl)-9-bromo-perylene-3,4-dicarboximide **(2),**[1]
6-bromo-2-(2,6-diisopropylphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione **(3),**[2]
2-(2,6-diisopropylphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione **(4),**[2] 4-(1,2,2-triphenylvinyl)phenylboronic acid **(TPE-B(OH)$_2$),**[5] and 4-(1,2,2-triphenylvinyl)phenol **(TPE-OH)**[6] were synthesized according to the literature published.
N-(2,6-diisopropylphenyl)-9-(4-N-(2,6-diisopropylphenyl)naphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide **(5),**[3]
N,N'-di(2,6-diisopropylphenyl)terrylene-3,4:11,12-tetracarboxdiimides **(6),**[3] and N,N'-di(2,6-diisopropylphenyl)-1,6,9,13-tetrabromo-terrylene-3,4:11,12-tetracarboxdiimides **(7)**[4] were prepared according to the previous literature with slight modifications.

N-(2,6-diisopropylphenyl)-9-(4-N-(2,6-diisopropylphenyl)naphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (5)

A mixture of compound **(2)** (2.5g, 4.46mmol), compound **(4)** (2.16g, 4.46mmol), K_2CO_3 (3.08g, 22.3mmol), toluene (160mL), water (80mL) and tetrabutylammonium hydrogen sulfate (TBAHS) (0.15g, 0.45mmol)

was added and the system was flushed with nitrogen. $Pd(PPh_3)_4$ (0.26g, 0.223mmol) was added and the reaction mixture was stirred under nitrogen at 80°C for 16h. After cooling down, the reaction mixture was extracted with dichloromethane (DCM), washed with water three times, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity silica-gel column chromatography eluting with DCM to yield the orange red solid (3.59g, 96.2%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.83 (d, 1H), 8.73 (dd, 3H), 8.67 (d, 1H), 8.60 (d, 1H), 8.58 – 8.54 (m, 2H), 7.98 (d, 1H), 7.91 (d, 1H), 7.74 – 7.67 (m, 2H), 7.58 – 7.47 (m, 5H), 7.37 (dd, 4H), 2.89 – 2.75 (m, 4H), 1.22 (dt,24H).

N,N'-di(2,6-diisopropylphenyl)terrylene-3,4:11,12-tetracarboxdiimides (TDI,6)

A mixture of compound **(5)** (3.5g, 4.18mmol), K_2CO_3 (3.2g, 22.7mmol) and ethanolamine (75mL) was added and the system was stirred under nitrogen at 135°C for 8h. After cooling to room temperature, the solution was poured into ethanol (200mL). The precipitate was collected by filtration, washed with water, dried under vacuum. The crude product was purified by gravity silica-gel column chromatography eluting with DCM to yield the blue product (3.31g, 94.8%). The analytical data corresponded to those in the literature.

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm):8.82 – 8.70 (m, 8H), 8.66 (d, 4H), 7.50 (t, 2H), 7.36 (d, 4H), 2.78 (dt, 4H), 1.22 (t, 24H).

N,N'-di(2,6-diisopropylphenyl)-1,6,9,13-tetrabromo-terrylene-3,4:11,12-tetracarboxdiimides (TDI-4Br,7)

TDI **(6)** (1.5g, 1.80mmol) was dissolved in chloroform (125mL) under slight heating. Bromine (1.85mL, 36.0mmol) was added and the reaction mixture was heated to reflux for 12h with exclusion of light. Chloroform and unreacted bromine were removed under vacuum. The crude product was purified by gravity silica-gel column chromatography eluting with DCM/petroleum ether (PE) (5:5, v/v) to yield the blue solid (1.15g, 55.6%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 9.55 (s, 4H), 9.01 (s, 4H), 7.51 (d, 2H), 7.37 (d, 4H), 2.76 – 2.70 (m, 4H), 1.20 (d, 24H).

N,N'-di(2,6-diisopropylphenyl)-1,6,9,13-tetra[4-(1,2,2-triphenylvinyl)phenyl]-terrylene-3,4:11,12-tetracarboxdiimides (TDI-4TPE)

A mixture of TDI-4Br **(7)** (0.20g, 0.174mmol), TPE-$B(OH)_2$ (0.39g, 1.04mmol), Na_2CO_3 (0.09g, 0.87mmol), dimethoxyethane (20mL) and water (5mL) was added and the system was flushed with nitrogen. $Pd(PPh_3)_4$ (0.01g, 0.009mmol) was added and the reaction mixture was stirred under nitrogen at 90°Cfor 24h. After cooling down, the reaction mixture was extracted with DCM, washed with water three times, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity silica-gel column chromatography eluting with DCM/PE (3:2, v/v) to yield the dark brown solid (0.19g, 50.7%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm):8.60 (s, 4H), 7.52 (d, 2H), 7.45 (s, 4H), 7.37 (d, 4H), 7.19 – 6.78 (m, 76H), 2.77 (dd, 4H), 1.20 (d, 24H). ^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm): 163.96, 145.68, 144.18, 143.52, 143.35, 143.30, 141.71, 140.80, 140.05, 139.63, 135.48, 134.15, 131.39, 131.28, 130.91, 129.97, 128.68, 127.86, 127.82, 127.73, 126.70, 124.07, 120.59, 29.70, 24.05. MS (MALDI-TOF, m/z): 2156.003 ($[M]^+$). Element analysis calcd. for $C_{162}H_{118}N_2O_4$ (%): C 90.22, H: 5.51, N 1.30; found C 89.97, H 5.55, N 1.31. HPLC purity: 98.45%.

N,N'-di(2,6-diisopropylphenyl)-1,6,9,13-tetra[4-(1,2,2-triphenylvinyl)hydroxyphenyl]-terrylene-3,4:11,12-tetracarboxdiimides (TDI-O-4TPE)

A mixture of TDI-4Br **(7)** (0.15g, 0.13mmol), TPE-OH (0.36g, 1.04mmol), K_2CO_3 (0.09g, 0.65mmol) and N-methyl-2-pyrrolidone (25mL) was added and the system was stirred under nitrogen at 80°C for 14h. After cooling to room temperature, water and conc. hydrochloric acid were added and the precipitate was collected by filtration, washed with water, dried under vacuum. The crude product was purified by gravity silica-gel column chromatography eluting with DCM/PE (3:2, v/v) to yield the blue product (0.08g, 27.6%). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 9.40 (s, 4H), 8.27 (s, 4H), 7.52 (dd, 2H), 7.36 (d, 4H), 7.08 (ddd, 48H), 7.00 (dd, 16H), 6.95 (t, 4H), 6.91 (d, 8H), 2.76 (dt, 4H), 1.20 (d, 24H). ^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm): 162.94, 154.55, 153.97, 145.72, 143.48, 143.41, 143.35, 141.42, 140.31, 139.75, 133.33, 131.37, 131.30, 131.28, 130.76, 128.80, 127.78, 127.64, 126.57, 126.49, 125.85, 124.04, 123.51, 122.05, 118.68, 29.70, 24.08. MS (MALDI-TOF, m/z): 2220.031 ($[M]^+$). Element analysis calcd. for $C_{162}H_{118}N_2O_8$ (%): C 87.62, H: 5.36, N 1.26; found C 87.44, H 5.39, N 1.30. HPLC purity: 99.36%.

2. HPLC SPECTRA.

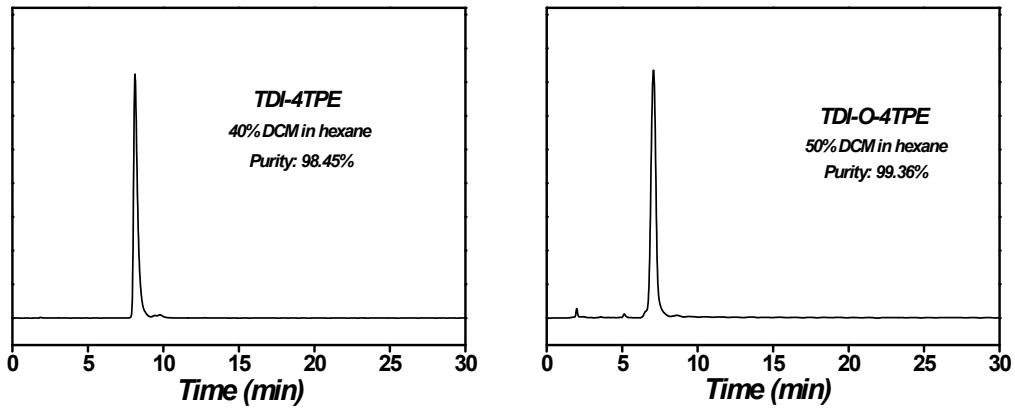


Fig. S1 The HPLC curves of TDI-4TPE and TDI-O-4TPE. The eluents are DCM/hexane binary mixed solvents

3. DENSITY FUNCTIONAL THEORY CALCULATIONS

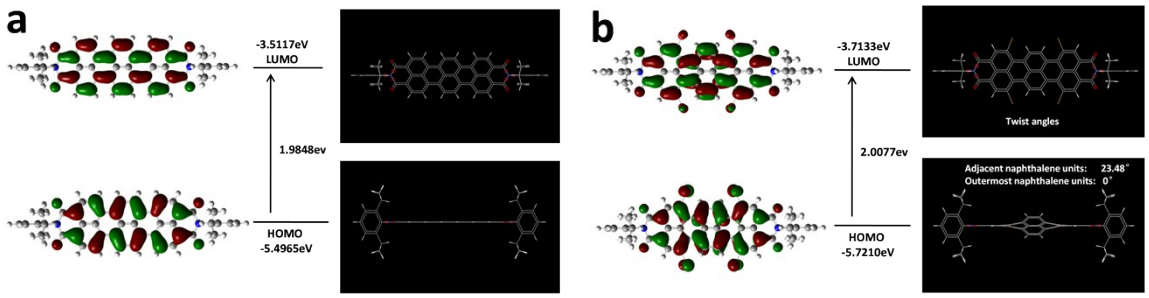


Fig. S2 HOMO and LUMO energy levels of (a) TDI and (b) TDI-4Br. Molecular orbital amplitude plots of HOMO and LUMO energy levels calculated using B3LYP/6-31G(d) basis set in Gaussian 09 program. Eg (energy gap) = LUMO - HOMO.

4. FLUORESCENCE QUANTUM YIELDS OF TDI-4TPE AND TDI-O-4TPE IN DIFFERENT SOLVENTS

Table S1 The fluorescence quantum yields in different solvents

Solvents	Hexane[a]	toluene	THF	chloroform	DMF
4TPE-TDI	0.39	0.30	0.16	0.18	0.03
4TPEO-TDI	0.84	0.79	0.37	0.49	0.06

The relative fluorescence quantum yields were estimated using TDI in chloroform (Φ_F = 0.9) [4] as standard. [a] :aggregate.

5. UV AND FL SPECTRA OF TDI-4TPE AND TDI-O-4TPE IN WATER-THF MIXTURES

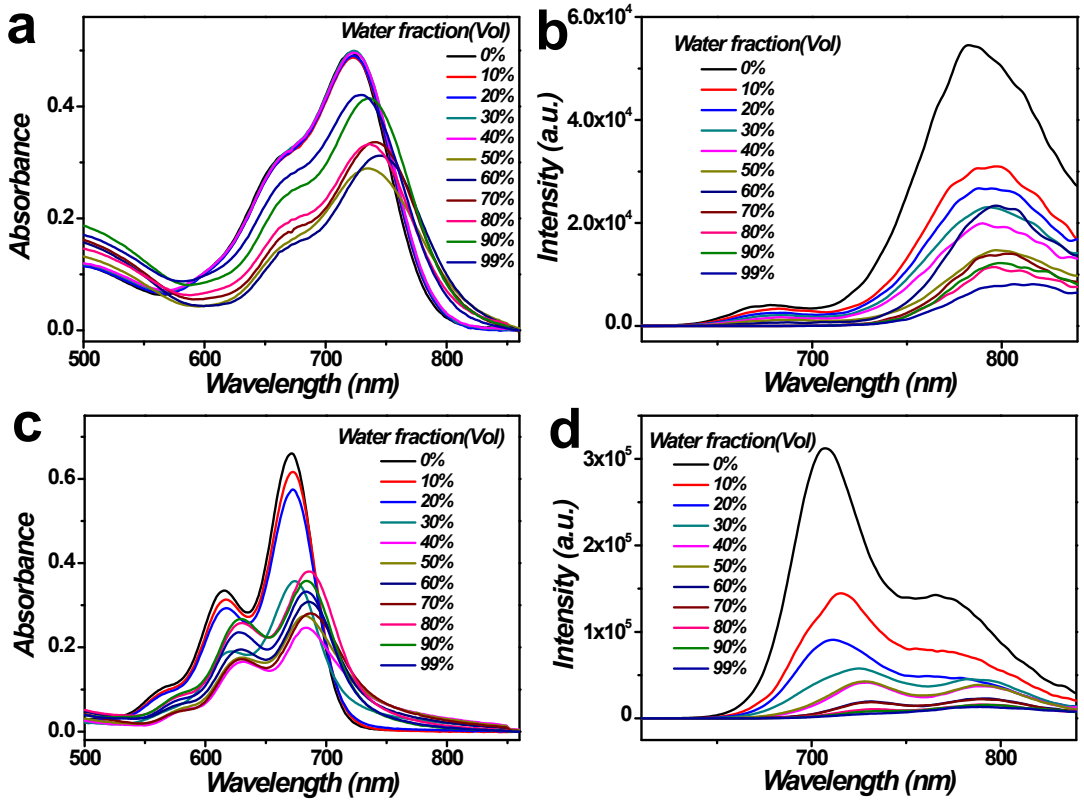


Fig. S3 Optical properties of TDI-4TPE and TDI-O-4TPE in water-THF binary solvents with different water fractions (by volume%)**.** (a) Absorption and (b) fluorescence spectra of TDI-4TPE. (c) Absorption and (d) Fluorescence spectra of TDI-O-4TPE . Concentration : 1.0 x 10^{-5}M, Excitation: 600nm.

6. FL SPECTRA OF POWDER SAMPLES

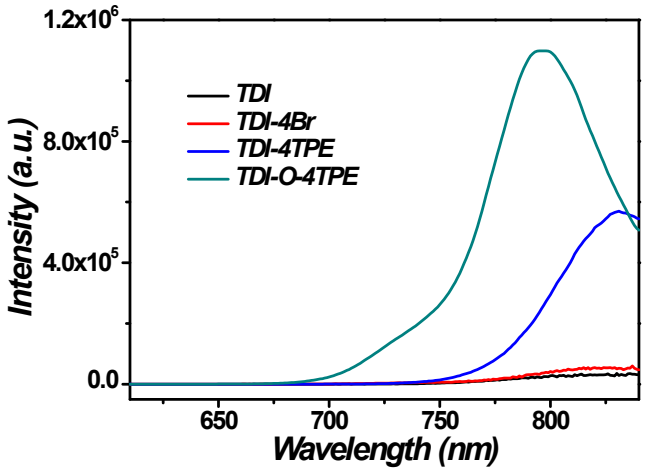


Fig. S4 Fluorescence spectra of TDI, TDI-4Br, TDI-4TPE, TDI-O-4TPE powders . The excitation wavelength is 600 nm.

7. PHOTOSTABILITY OF TDI-4TPE AND TDI-O-4TPE

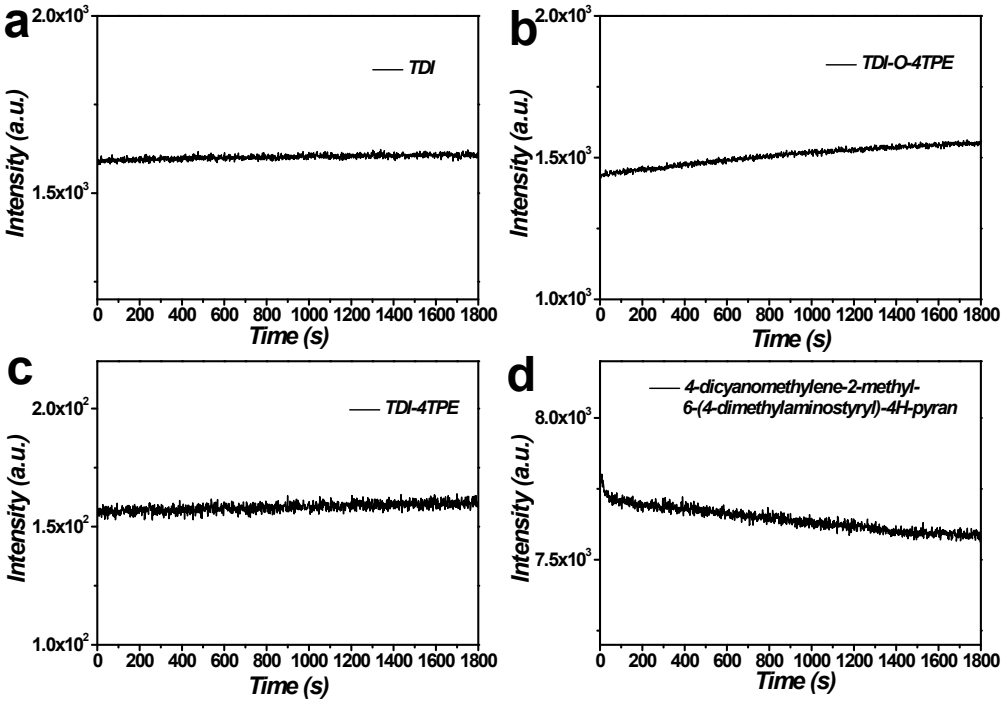


Fig. S5 The fluorescence intensity of dyes in PS film under persistent 600 nm (a-c) or 480 nm (d) visible light irradiation. The monitored emission wavelength: (a) TDI, 670nm; (b) TDI-O-4TPE, 700nm; (c) TDI-4TPE, 780nm; (d) 4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran, 630nm.

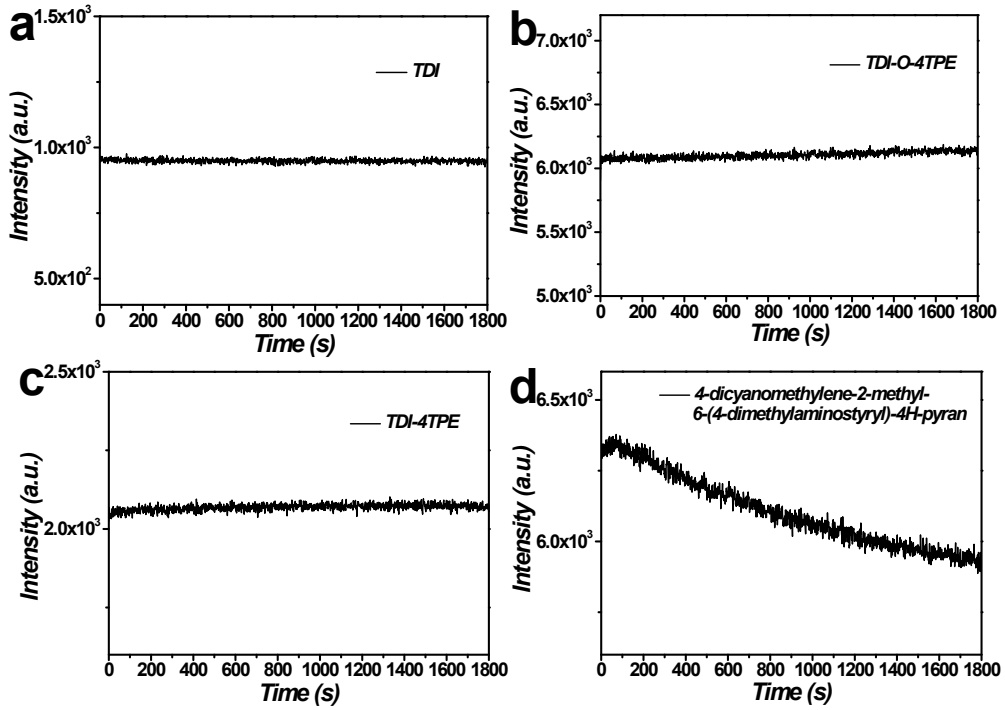


Fig. S6 The fluorescence intensity of dyes in PS film under persistent 302 nm UV light irradiation. The monitored emission wavelength: (a) TDI, 670nm; (b) TDI-O-4TPE, 700nm; (c) TDI-4TPE, 780nm; (c) 4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran, 630nm.

8. TYNDALL EFFECT OF TDI-4TPE AND TDI-O-4TPE IN 99% HEXANE/DCM.

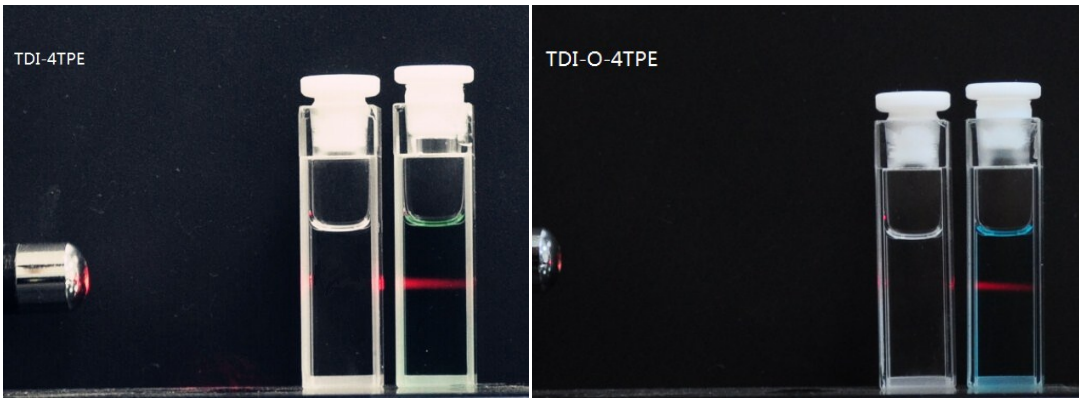


Fig. S7 The demonstrative experiment of Tyndall effect of TDI-4TPE and TDI-O-4TPE in 99% hexane fraction in DCM. The left cuvette in each picture is filled with the solvent without dyes as a blank, while the right one is filled with dyes. A red laser pen passes through the samples from the left. The concentrations of dyes are 1.0 x 10^{-5}M.

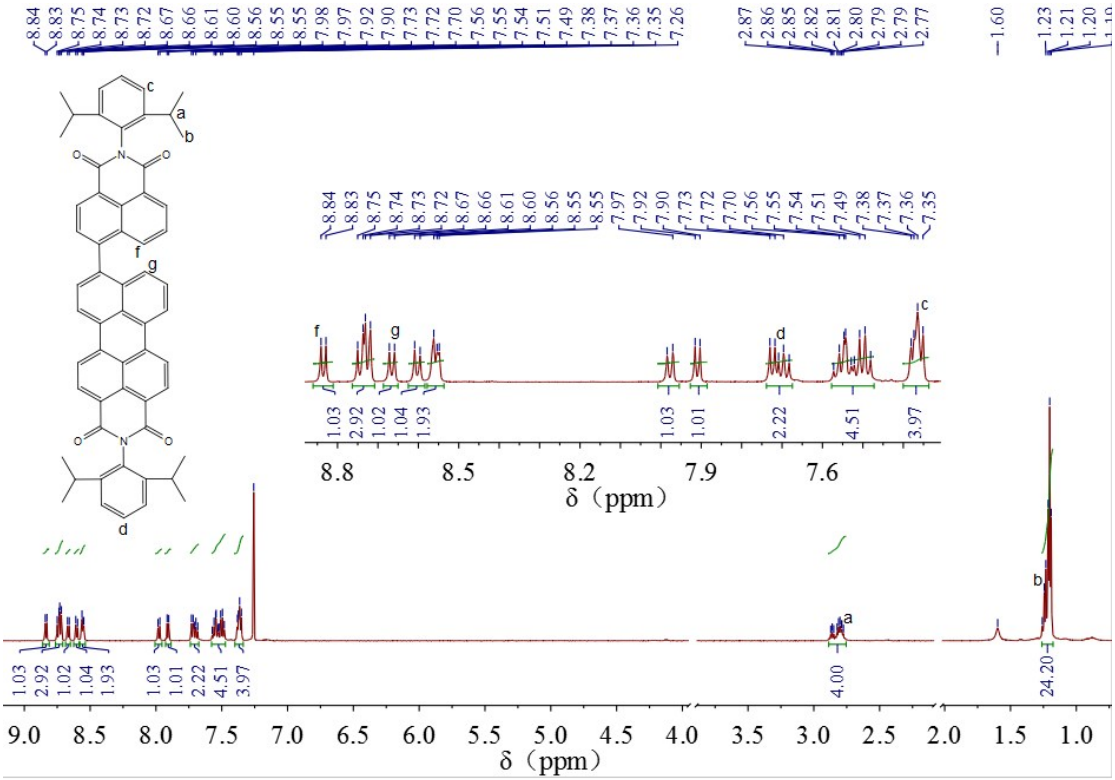
9. LIFETIME OF TDI-4TPE AND TDI-O-4TPE.

Table S2 Fluorescence Lifetimes of TDI-4TPE and TDI-O-4TPE in solutions

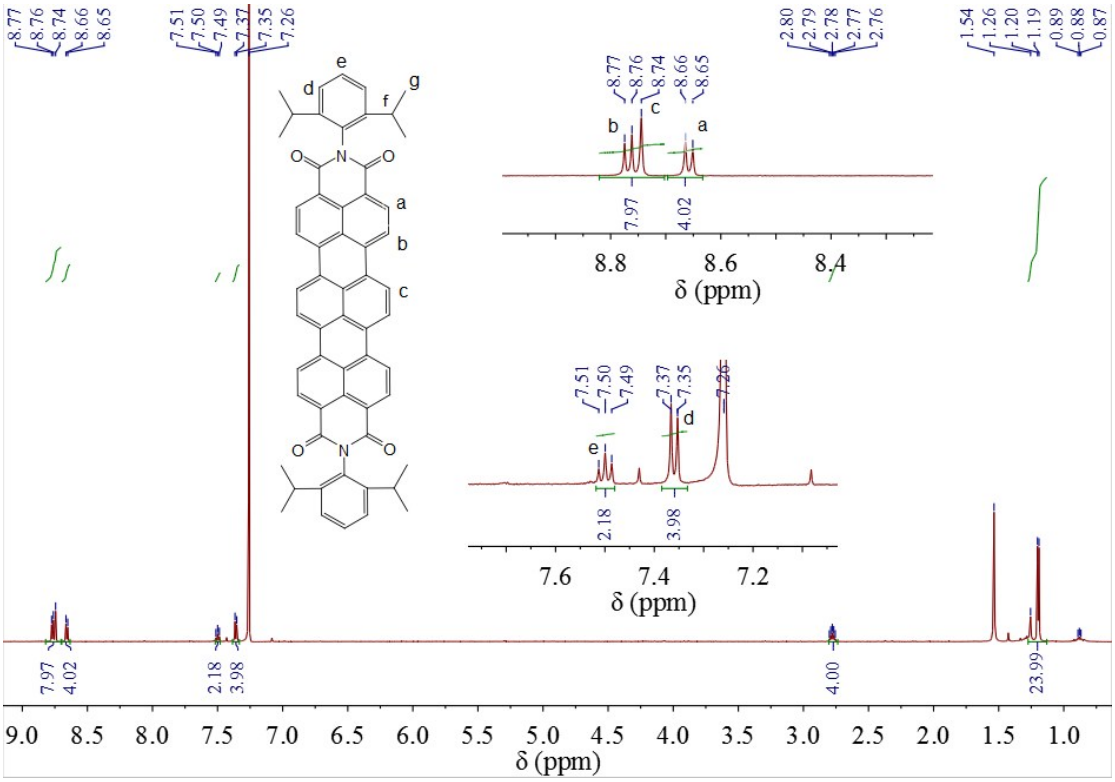
Solvents	TDI-4TPE			TDI-O-4TPE		
	τ_1(ns)	τ_2(ns)	χ^2	τ_1(ns)	τ_1(ns)	χ^2
Cyclohexane	4.49	-	1.054	3.99	-	1.005
DCM	1.99	-	1.289	1.35	-	1.371
DMF	0.63(93.63)	4.83(6.37)	1.060	0.55(94.29)	2.21(5.71)	1.246

10. NMR SPECTRA.

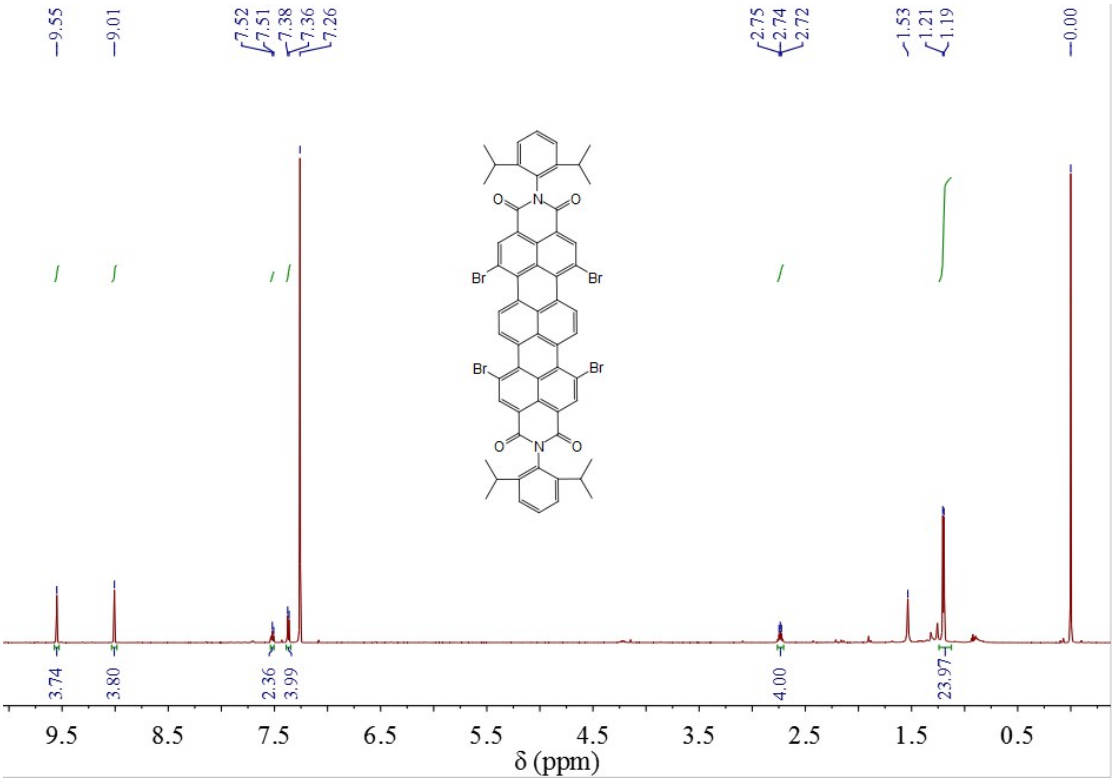
Compound **5**



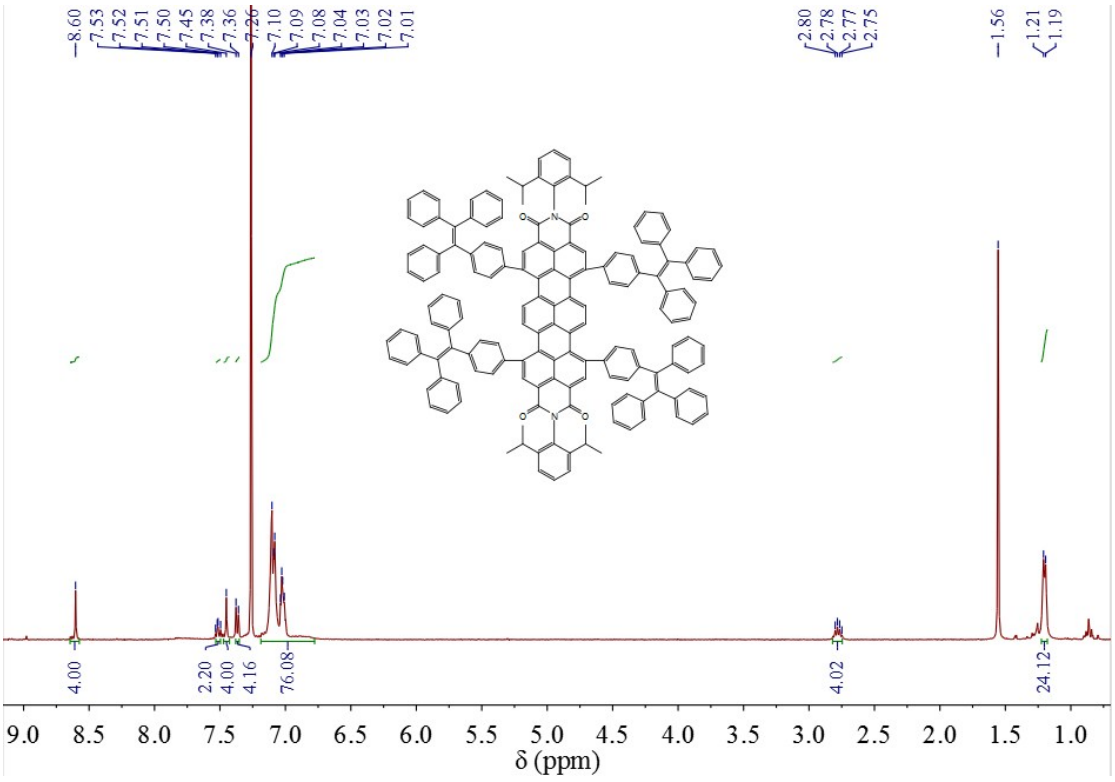
TDI

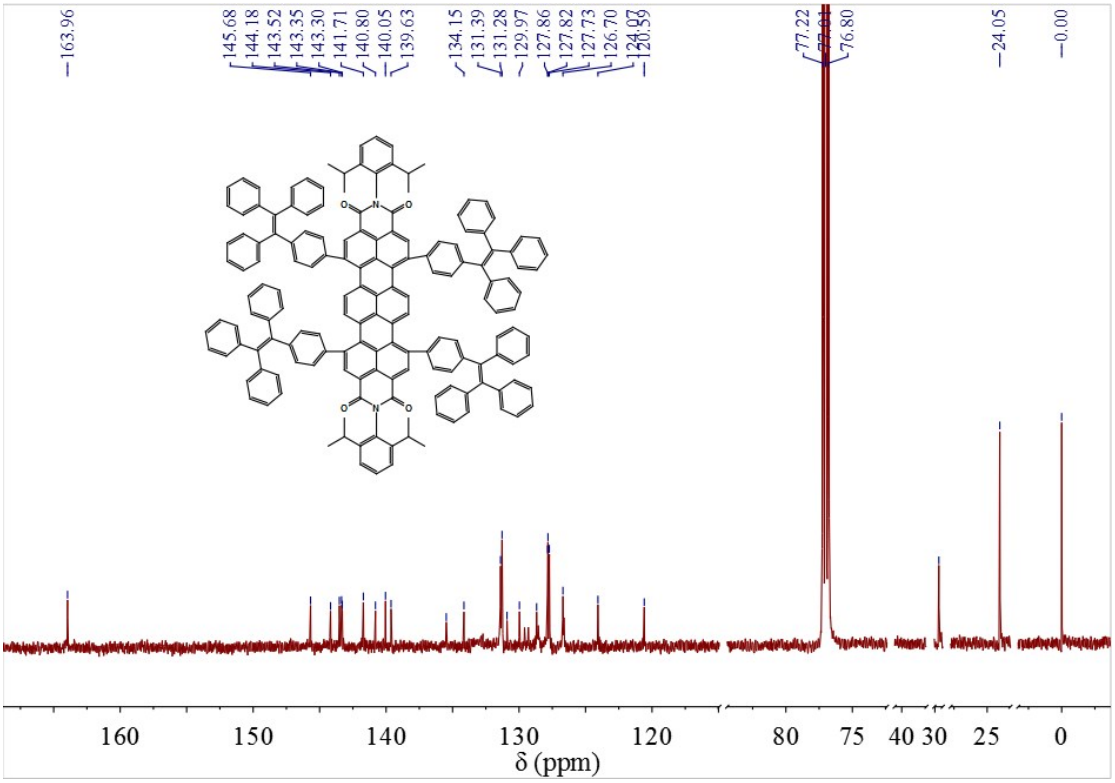


TDI-4Br

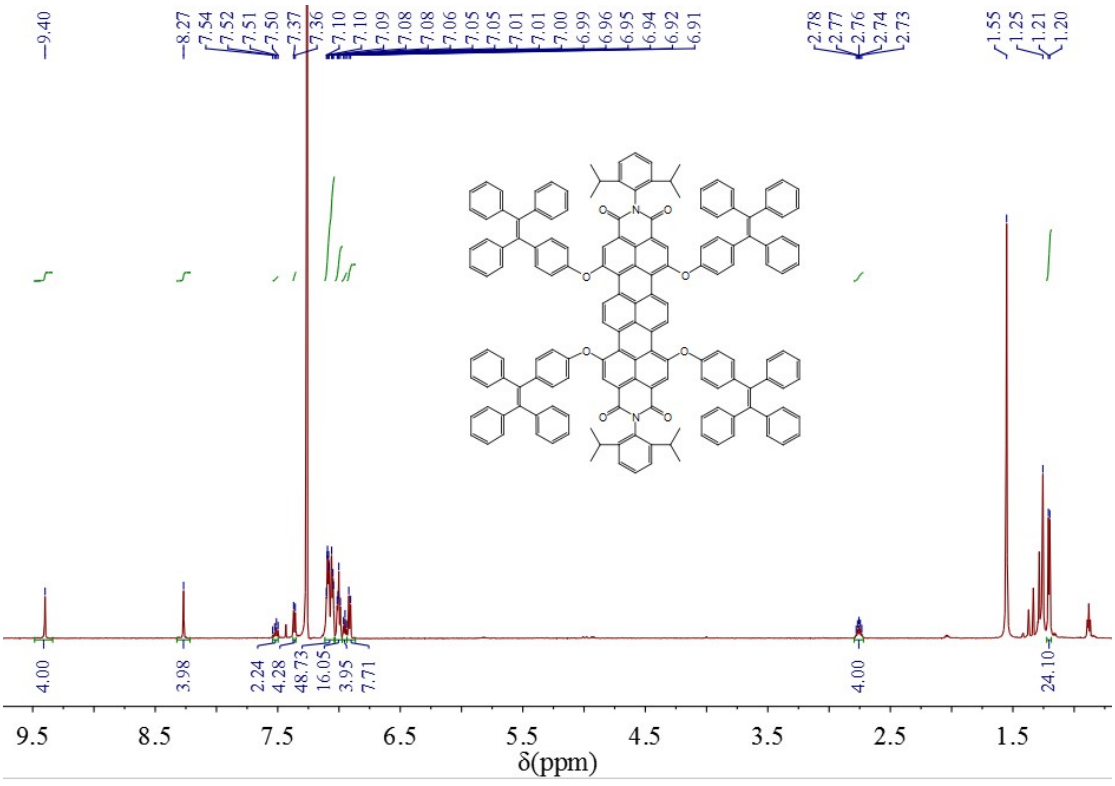


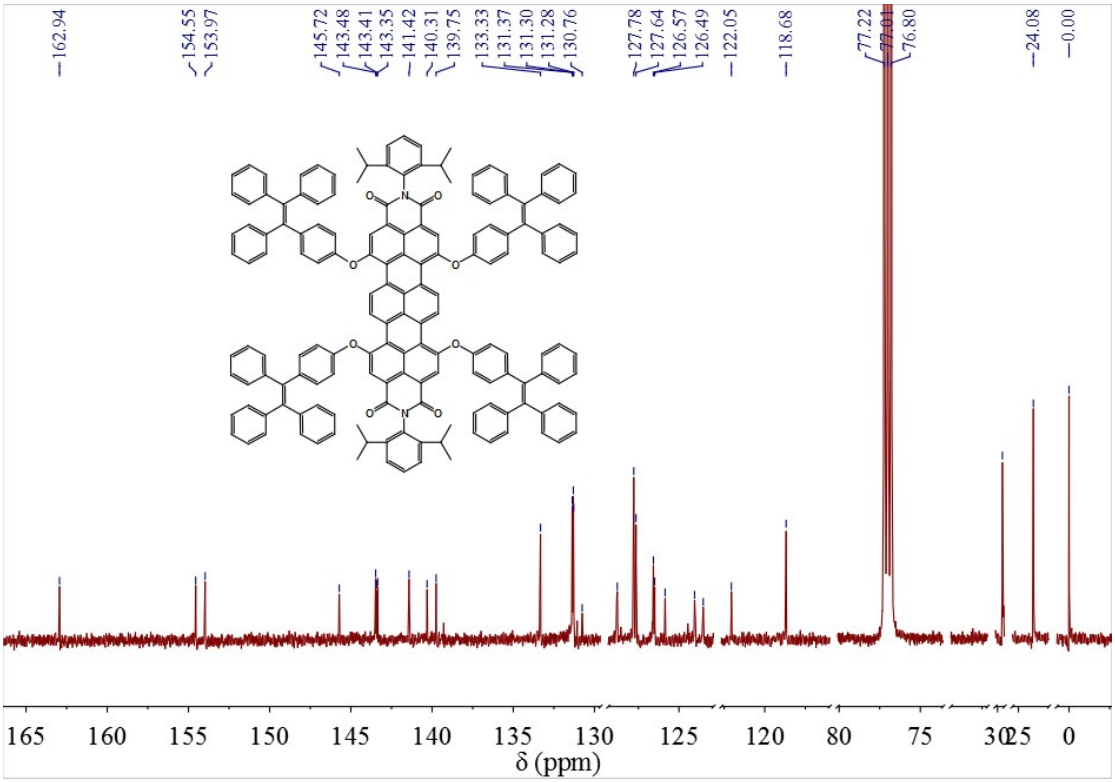
TDI-4TPE




163.96
145.68
144.18
143.52
143.35
143.30
141.71
140.80
140.05
139.63
134.15
131.39
131.28
129.97
127.86
127.82
127.73
126.70
124.07
120.59
77.22
76.80
24.05
0.00
160
150
140
130
120
80
75
40 30
25
0
δ (ppm)

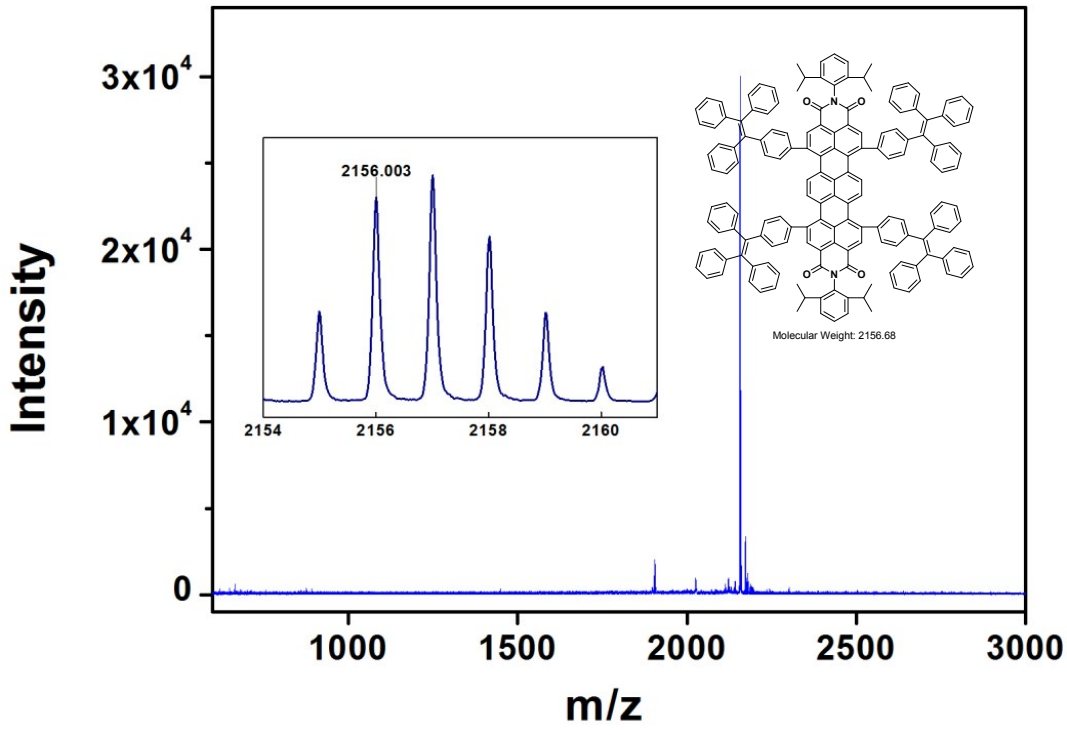
TDI-O-4TPE


9.40
8.27
7.54
7.52
7.51
7.50
7.37
7.36
7.10
7.10
7.09
7.08
7.08
7.06
7.05
7.05
7.01
7.01
7.00
6.99
6.96
6.95
6.94
6.92
6.91
2.78
2.77
2.76
2.74
2.73
1.55
1.25
1.21
1.20
4.00
3.98
2.24
4.28
48.73
16.05
3.95
7.71
4.00
24.10
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
δ(ppm)

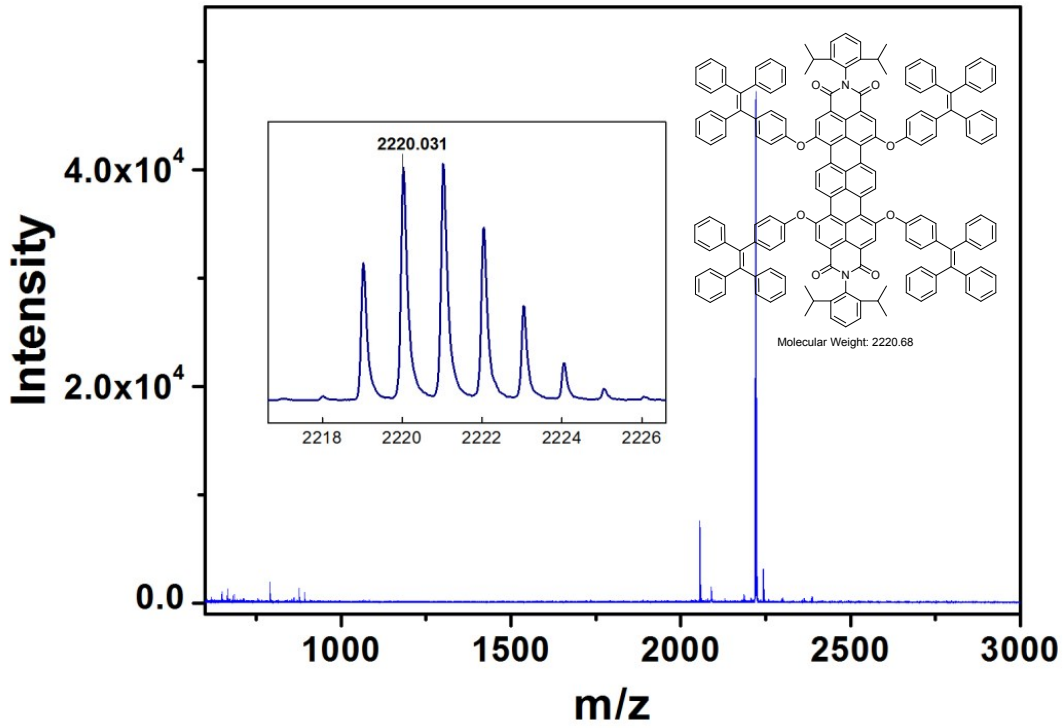


11. MASS SPECTRA.

TDI-4TPE



TDI-O-4TPE



12. REFERENCES.

[1] (a) L. Feiler, H. Langhals, K. Polborn, *Liebigs Ann.* **1995**, 1229-1244. (b) Y. Geerts, H. Quante, H. Platz, R. Mahrt, M. Hopmeier, A. Böhm, K. Müllen, *J. Mater. Chem.* **1998**, *8*, 2357–2369. (c) C. Li, H. Yan, G. F. Zhang, W. L. Gong, T. Chen, R. Hu, M. P. Aldred, M. Q. Zhu, *Chem. Asian J.***2014**, *9*, 104-109.

[2] G. F. Zhang, H. F. Wang, M. P. Aldred, T. Chen, Z. Q. Chen, X. G. Meng, M. Q. Zhu, *Chem. Mater*. **2014**, *26*, 4433-4446.

[3] (a) F. Holtrup, G. Müller, H. Quante, S. de Feyter, F. C. De Schryver, K. Müllen, *Chem. Eur. J.***1997**, *3*, 219-225. (b) F. Nolde, J. Q. Qu, C. Kohl, N. Pschirer, E. Reuther, K. Müllen, *Chem. Eur. J*. **2005**, *11*, 3959-3967.

[4] T. Weil, E. Reuther, C. Beer, K. Müllen, *Chem. Eur. J*. **2004**, *10*, 1398-1414.

[5] (a) G. F. Zhang, M. P. Aldred, W. L. Gong, C. Li, M. Q. Zhu, *Chem. Comm.,***2012**, *48*, 7711-7713. (b) M. P. Aldred, C. Li, G. F. Zhang, W. L. Gong, A. D. Q. Li, Y. Dai, D. Ma, M. Q. Zhu, *J. Mater. Chem.,***2012**, *12*, 7515-7528.

[6] Q. L. Zhao, K. Li, S. J. Chen, A. J. Qin, D. Ding, S. Zhang, Y. Liu, B. Liu, J. Z. Sun, B. Z. Tang, *J. Mater. Chem.***2012**, *22,* 15128-15135.