Aggregation-Induced Red Emission of Tetraphenylethene Modified Perylene Bisimide: Effect of Substitution on Fluorescent Performance

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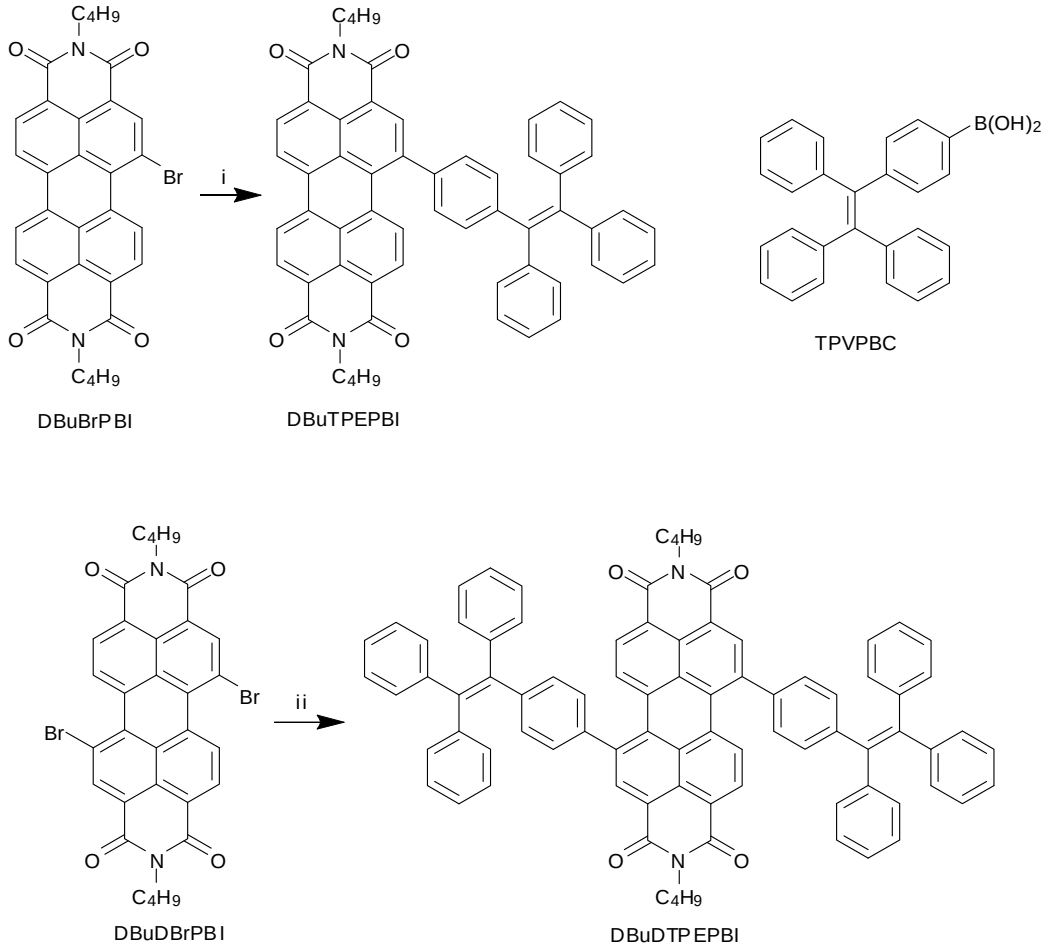
Experimental Section

Materials: All the chemicals used were purchased from Across or Alfa, unless specifically stated. Bromine was purchased from Alladin. THF was distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. All other solvents were of analytical grade and were purified using standard methods. *N,N′*-dibutyl-perylene-3,4:9,10-tetracarboxylic acid bisimide (DBuPBI), and *N,N′*-dibutyl-1-bromoperylene-3,4:9,10-tetracarboxylic acid bisimide (DBuBrPBI) were synthesized according to literature procedure.[1] *N,N′*-Dibutyl-1,7- and -1,6-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (DBuDBrPBI) was synthesized according to literature procedure.[2] The intermediate of 4-(1,2,2-triphenyvinyl) phenylboronic acid (TPVPBC) was prepared according to our previously published procedures.[3]

Instrumentation: ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 400 or 500 spectro- meter in $CDCl_3$ or DMSO-d_6. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. PL spectra were measured on a PL spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Φ_F values were estimated using Rodamin B in ethanol (Φ_F=70%) as standard. The absorbance of the solutions was kept between 0.04 and 0.06 to avoid the internal filter effect. Elemental analysis was performed on a ThermoFinnigan Flash EA1112. The fluorescence micrographs were taken on an inverted fluorescence microscope (Nikon Eclipse TE2000-U). Scanning electron microscope (SEM) images were taken on a JSM-5510 scanning electron microscopy.



Scheme S1 Synthetic routes to DBuTPEPBI and DBuDTPEPBI. Reagents and conditions: i) TPVPBC, $Pd(PPh_3)_4$, Na_2CO_3, THF, reflux, N_2, overnight; ii) TPVPBC, $Pd(PPh_3)_4$, Na_2CO_3, THF, reflux, N_2, 48h.

Synthesis of *N,N′-dibutyl-1-(4-(1,2,2-triphenyl)vinyl)phenylperylene-3,4:9,10–tetracarboxylic acid bisimide (*DBuTPEPBI*)*: In a 250 mL two-necked round-bottom flask, DBuBrPBI (0.019 g, 0.033 mmol) , TPVPBC (0.017 g, 0.037 mmol), and $Pd(PPh_3)_4$ (2 mg) were added. The flask was evacuated under vacuum and flushed with nitrogen three times. THF (20 mL) and 2 M Na_2CO_3 were injected to the flask. The mixture was refluxed for 24h. After cooled

to room temperature, the mixture were added to 80 mL water and extracted with DCM. The collected organic layer was dried over anhydrous magnesium sulfate. After solvent evaporation, the crude product was purified by a silica gel column using DCM/petroleum ether (2:1 by volume) as eluent and then was recrystallized from MeOH and chloroform three times. A dark red solid was obtained in 51% yield (0.014g). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.61-8.64 (m, 2H), 8.49-8.53 (m, 3H), 8.14-8.16 (d, J = 8.0Hz, 1H), 7.83-7.84 (d, J = 8.5Hz, 1H), 7.30-7.31 (m, 3H), 7.07-7.22 (m, 16H), 4.19-4.22 (m, 4H), 1.73-1.76 (m, 4H), 1.46-1.49 (m, 4H), 0.98-1.02 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 163.7, 163.6, 163.4, 144.9, 143.8, 143.5, 142.3, 141.7, 140.5, 140.2, 134.9, 134.8, 134.6, 133.6, 132.6, 131.6, 131.5, 129.0, 128.3, 128.2, 128.1, 127.9, 127.6, 127.0, 123.3, 123.2, 122.3, 40.6, 54.2, 30.4, 29.9, 20.6, 14.1. HRMS (MALDI-TOF, m/z): [M^+] calcd for $C_{58}H_{44}N_2O_4$: 832.3301, Found: 832.3303 (see Fig. S1). Anal. Calcd for $C_{58}H_{44}N_2O_4 \cdot H_2O$: C 81.86, H 5.45, N 3.29; found: C 81.92, H 5.52, N 3.21.

Synthesis of *N,N'-dibutyl-1,7-di(4-(1,2,2-triphenyl)vinyl)phenyl-perylene-3,4:9,10-tetracarboxylic acid bisimide* (DBuDTPEPBI): In a 250 mL two-necked round-bottom flask, DBuDBrPBI (0.2 g, 0.3 mmol), TPVPBC (0.3 g, 0.65 mmol), and $Pd(PPh_3)_4$ (35 mg) were added. The flask was evacuated under vacuum and flushed with nitrogen three times. THF (40 mL) and 2 M Na_2CO_3 were injected to the flask. The mixture was refluxed for 48h. After cooled to room temperature, the mixture were added to 80ml water and extracted with DCM. The collected organic layer was dried over anhydrous magnesium sulfate. After solvent evaporation, the crude product was purified by a silica gel column using DCM/petroleum ether (3:2 by volume) as eluent. A dark red solid was obtained in 44% yield (0.152 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.52 (s, 2H), 8.11-8.13 (d, J = 8.5 Hz, 2H), 7.73-7.74 (d, J = 8.0 Hz, 2H), 7.06-7.31 (m, 38H), 4.21-4.24 (m, 4H), 1.71-1.77 (m, 4H), 1.43-1.51 (m, 4H), 0.99-1.02 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 163.7, 163.6, 144.8, 143.9, 143.6, 142.3, 141.1, 140.3, 135.3, 134.9, 133.4, 132.6, 131.6, 130.3, 129.4, 128.6, 128.3, 128.2, 127.9, 127.3, 127.0, 122.4, 122.0, 40.6, 30.5, 20.6, 14.1. HRMS (MALDI-TOF, m/z): [M^+] calcd for $C_{84}H_{62}N_2O_4$: 1162.4710, Found: 1162.4709 (see Fig. S2). Anal. Calcd for $C_{84}H_{62}N_2O_4$: C 86.72, H 5.37, N 2.41; found: C 86.29, H 5.94, N 2.19.

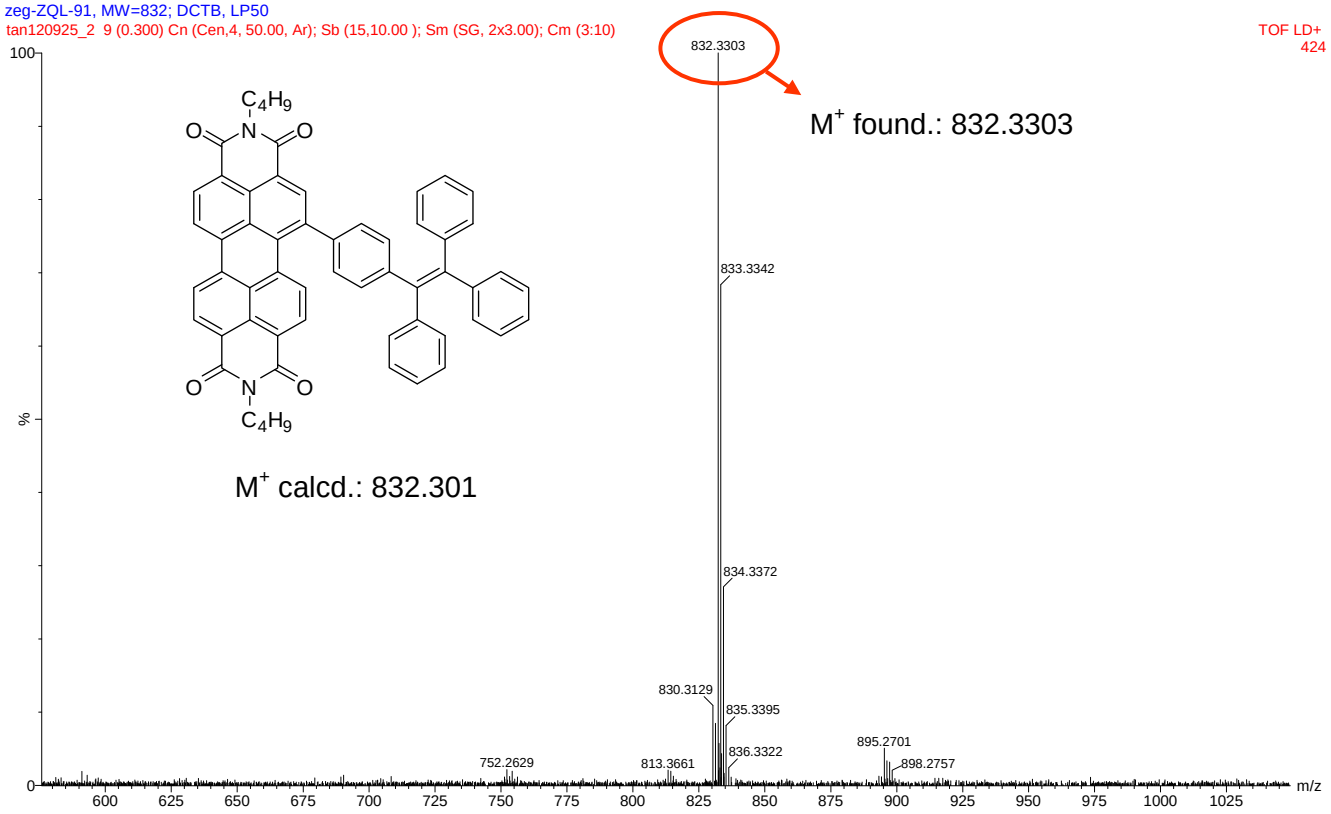


Fig. S1. High resolution mass spectrum of DBuTPEPBI.

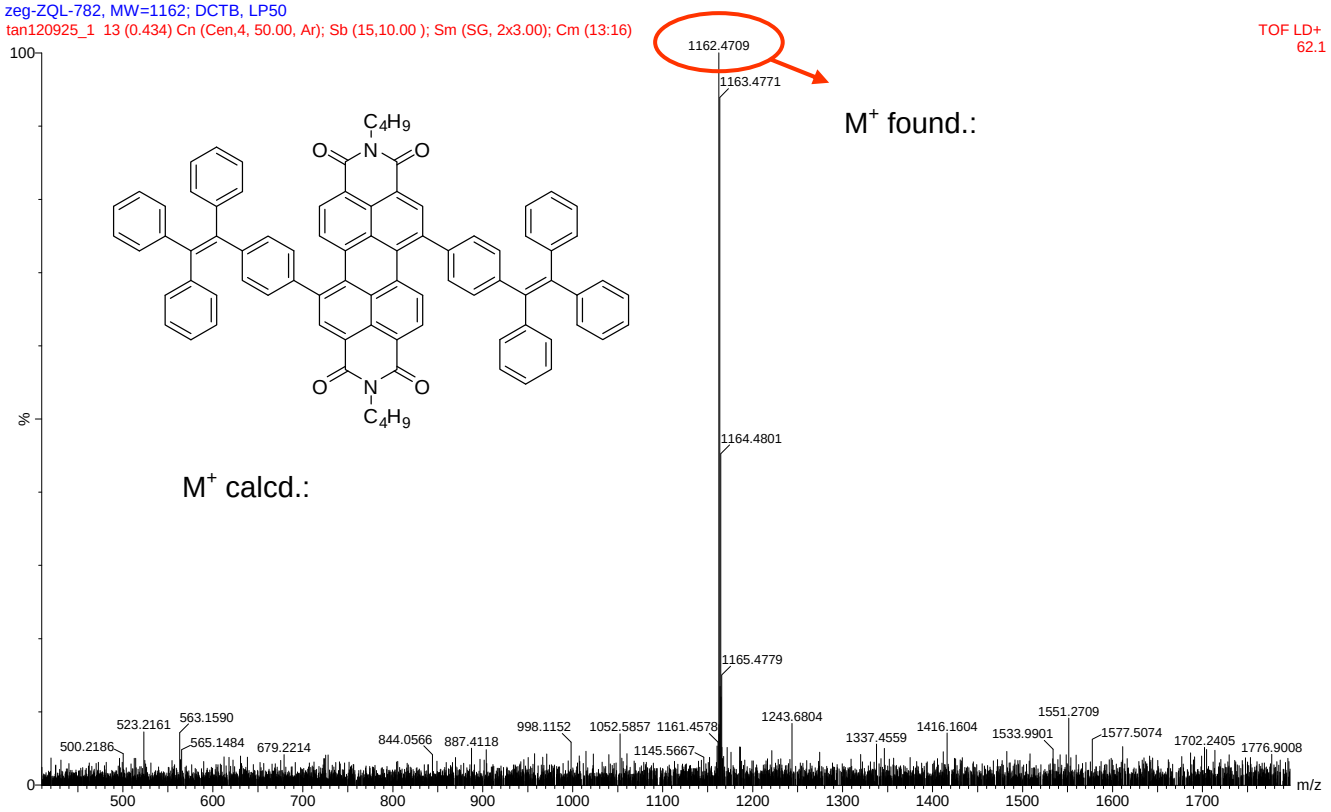


Fig. S2. High resolution mass spectrum of DBuDTPEPBI.

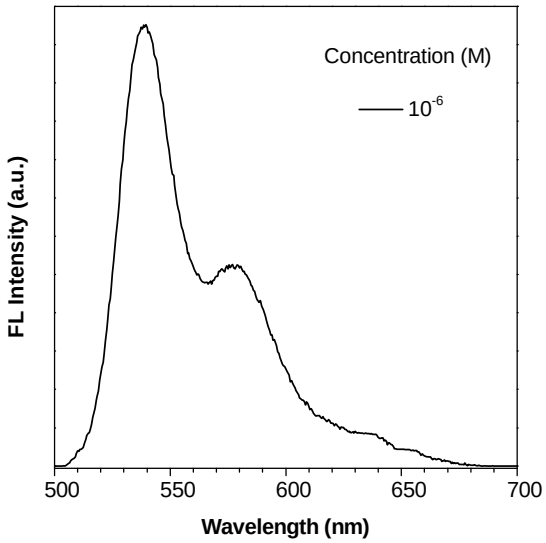


Fig. S3 Emission spectrum of compound DBuBrPBI in DCM solution. Concentration: 10^{-6} M. Excitation at 486 nm.

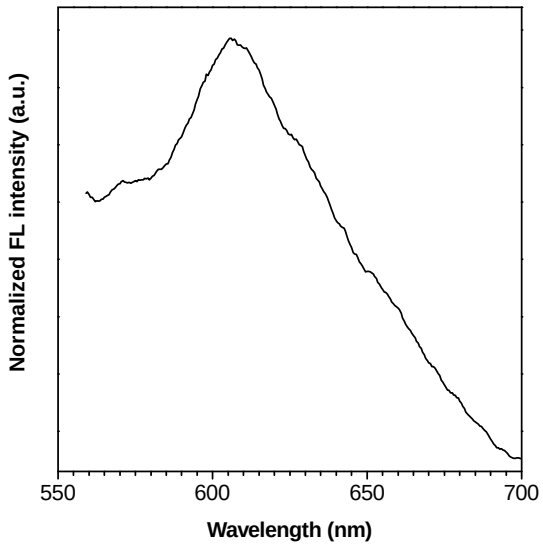


Fig. S4 Normalized FL spectra of DBuBrPBI in solid state.

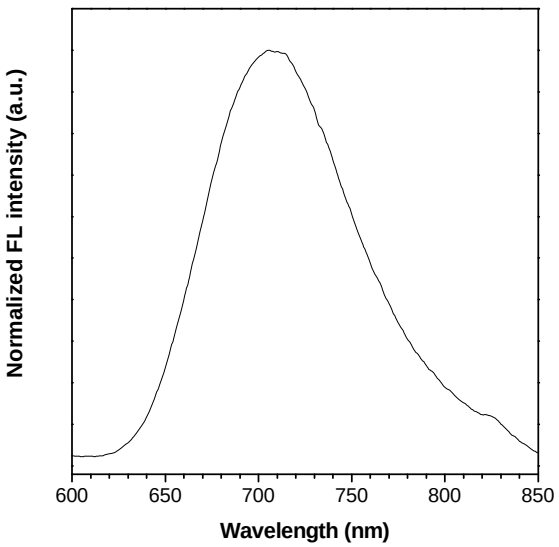


Fig. S5 Normalized FL spectra of DBuDTPEPBI in solid state.

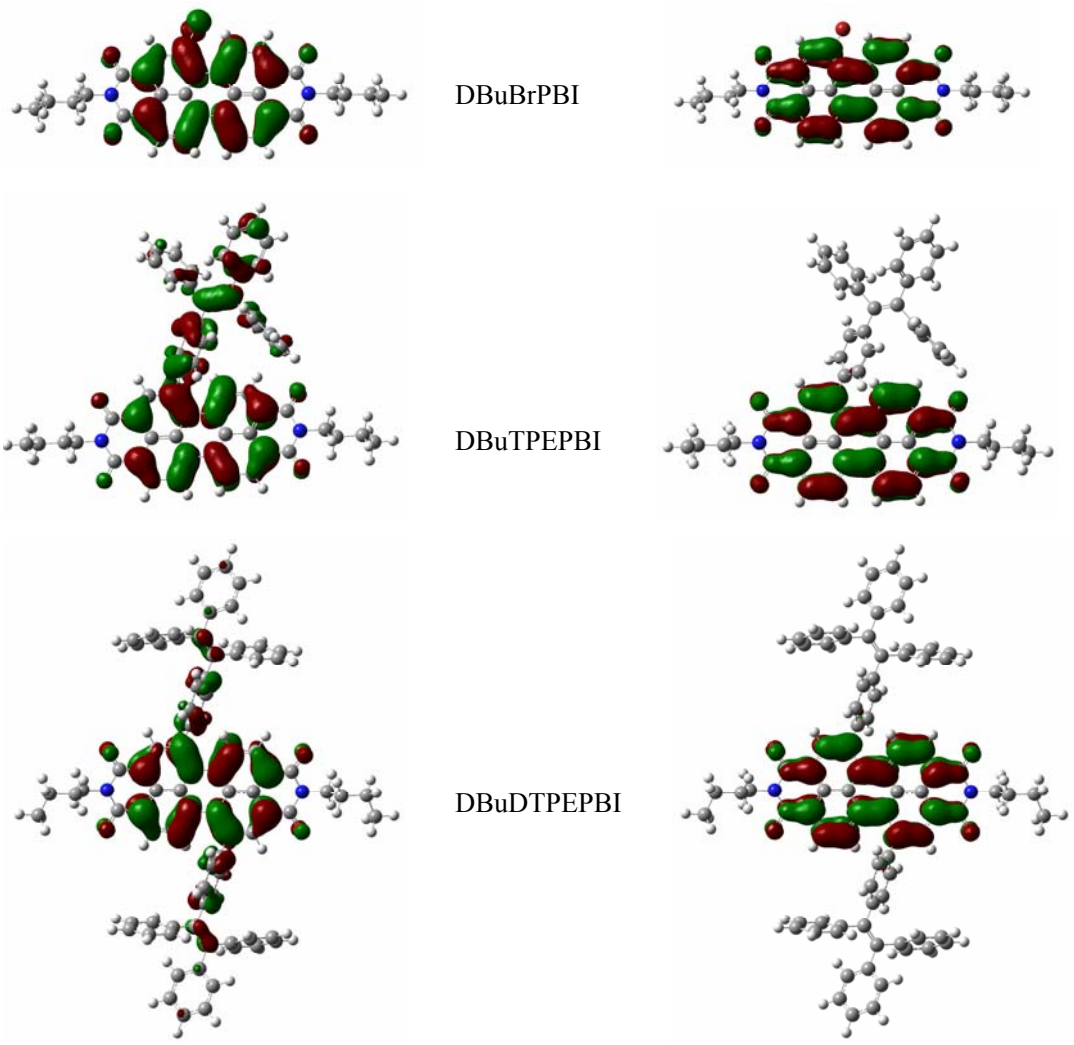


Fig. S6 Optimal molecular orbital amplitude plots of HOMO and LUMO levels of DBuBrPBI, DBuTPEPBI and DBuDTPEPBI. The white, grey, blue and red balls represent H, C, N and O atoms, respectively.

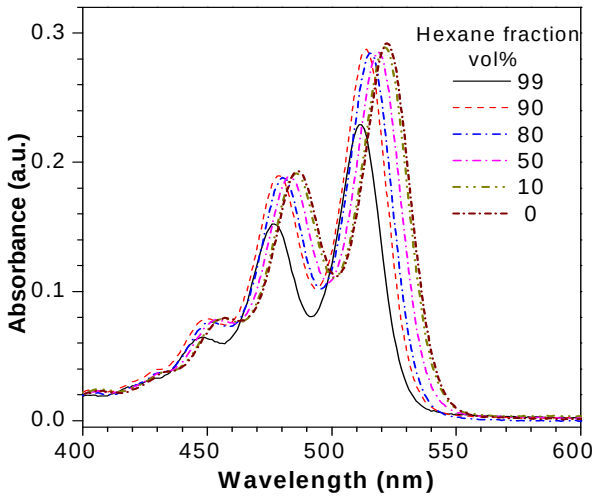


Fig. S7 Absorption spectra of compound DBuBrPBI in hexane/DCM mixtures with different hexane contents (V:V). Concentration: 10^{-5}M.

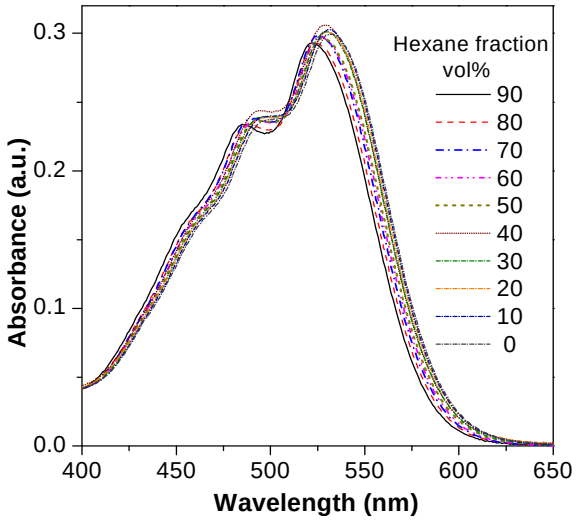


Fig. S8 Absorption spectra of compound DBuTPEPBI in hexane/DCM mixtures with different hexane contents (V:V). Concentration: 10^{-5}M.

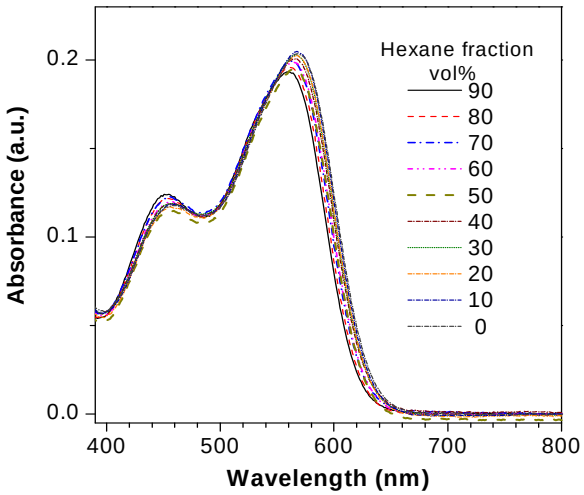


Fig. S9 Absorption spectra of compound DBuDTPEPBI in hexane/DCM mixtures with different hexane contents (V:V). Concentration: 10^{-5}M.

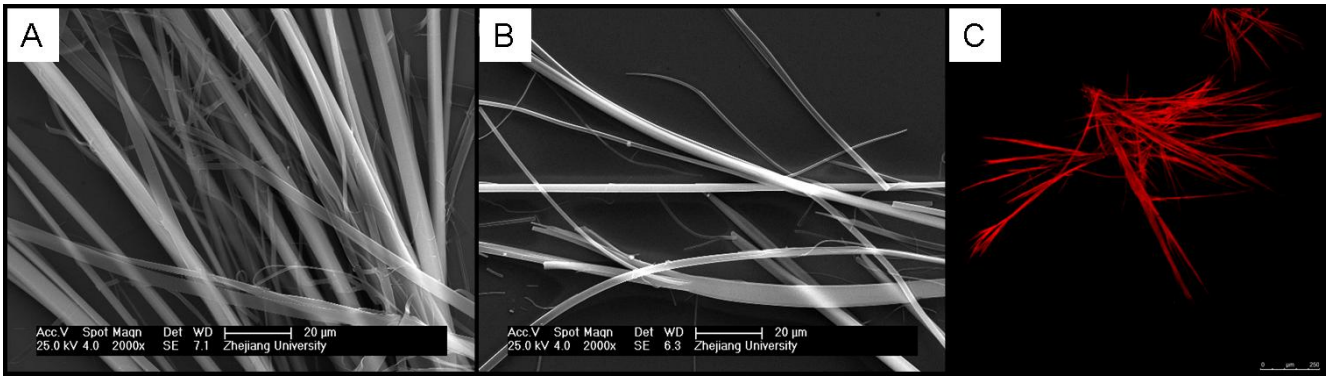


Figure S10 (A) and (B) display SEM images of the morphologies of the aggregates formed by DBuTPEPBI molecules in different MeOH/DCM mixtures, (A) 80% and (B) 90% MeOH contained in the mixtures, respectively. (C) displays the confocal fluorescence images corresponding to the microstructures in (A).

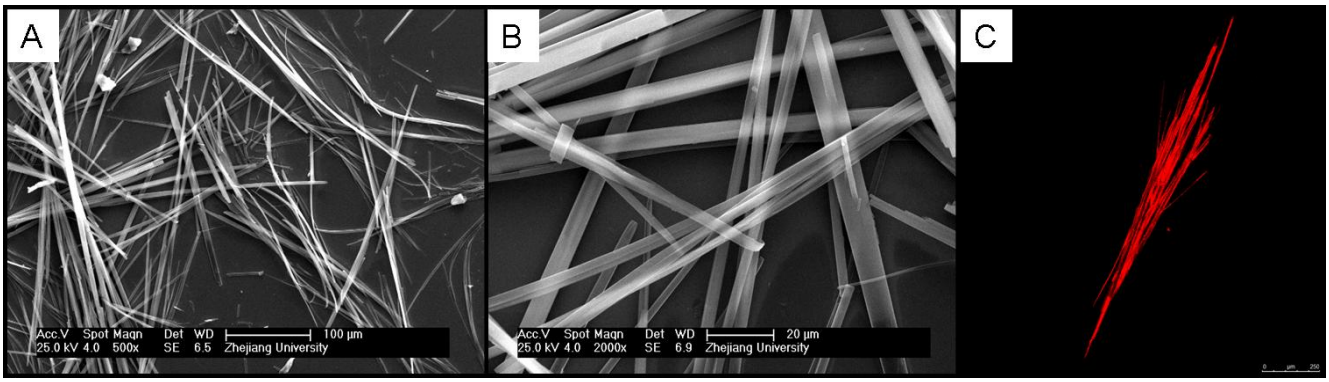


Figure S11 (A) and (B) display SEM images of the morphologies of the aggregates formed by DBuDTPEPBI molecules in 80% MeOH contained MeOH/DCM mixtures. (C) displays the confocal fluorescence images corresponding to the microstructures in (A).

References

1. P. Rajasingh, R. Cohen, E. Shirman, L. J. Shimon and B. Rybtchinski, *J Org Chem*, 2007, **72**, 5973-5979.
2. F. Wurthner, V. Stepanenko, Z. Chen, C. R. Saha-Moller, N. Kocher and D. Stalke, *J Org Chem*, 2004, **69**, 7933-7939.
3. W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma, B. Z. Tang, *Adv. Mater.* 2010, **22**, 2159.