

Supporting Information for

Fully Conjugated Tri(perylene bisimides) : an Approach to Construction
of *n*-Type Graphene Nanoribbons

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Materials and Methods:

¹H NMR and ¹³C NMR spectra were recorded in deuterated solvents on a Bruker DMX 300 NMR Spectrometer and a Bruker ADVANCE 600 NMR Spectrometer. ¹H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX Mass Spectrometer.

N,N'-di(2,6-diisopropylphenyl)-1,6,7,12-tetrabromoperylene-3,4:9,10-tetracarboxylicbisimides were prepared according to a known procedure.¹ All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. DMSO was freshly distilled from CaH₂. Two isomers of tri(perylene bisimides) were separated by HPLC using Cosmosil Buckyprep as the column and toluene as the eluent.

Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammograms (CVs) were recorded on a CHI66 electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in CH₂Cl₂ was employed as the supporting electrolyte. CH₂Cl₂ was freshly distilled prior to use. The reduction potentials have been recalculated to the reference of Fc/Fc⁺. The energy level of Fc/Fc⁺ is assumed to be -4.8 eV below the vacuum level.² The oxidation potential of Fc/Fc⁺ was measured as 0.40 V against Ag/AgCl.

Synthesis and Characterization of triPBIs:

triPBIs 5 and 6.

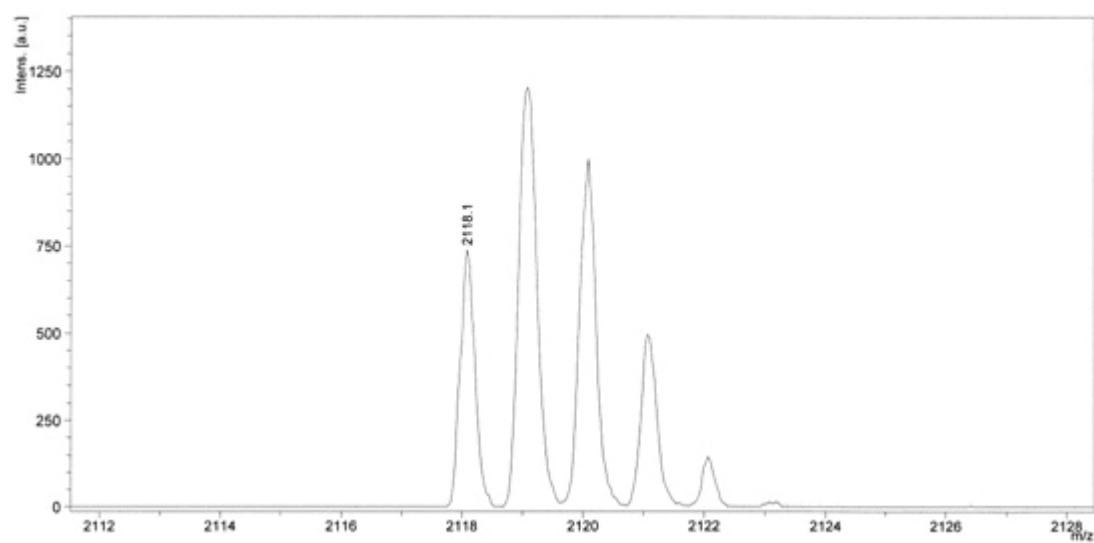
A mixture of tetrabromoperylene bisimide (634 mg, 0.62 mmol), CuI (706 mg, 3.72 mmol), L-proline (500 mg, 4.35 mmol), K₂CO₃ (856 mg, 6.2 mmol) in 10 ml DMSO was heated at 110 °C under Ar for 12 h. The cooled mixture was poured into 1M HCl, and stirred for 1 hr. After filtration, the obtained solids were washed with brine, dried under vacuum, dissolved in CH₂Cl₂, and purified by column chromatography (silica gel, CH₂Cl₂). Yield 65 mg (15%) **diPBI** as black

solids and 70 mg (16%) **triPBIs** as dark-green solids. The obtained **triPBIs** were separated by HPLC into two fractions using Cosmosil Buckyprep as the column and toluene as the eluent. After separation, triPBI **5** (18 mg) and **6** (52 mg) were obtained, in total yield of 4% and 12%, respectively. MS (MALDI-TOF): calcd for **triPBI** C₁₄₄H₁₁₄N₆O₁₂, 2118.8 [M]⁺; found, triPBI **5** *m/z* = 2118.1; triPBI **6** *m/z* = 2118.2.

triPBI 5. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ = 10.81 (s, 2H), 10.24 (s, 2H), 9.56 (m, 4H), 9.45 (d, 2H), 9.21 (d, 2H), 7.40-7.60 (m, 18H), 2.62-3.06 (b, 12H), 0.98 (m, 24H), 0.86 (m, 48H). ¹³C NMR of **5** can not be well resolved.

triPBI 6. ¹H NMR (1,2-dichlorobenzene-d₄, 300 MHz, 383 K): δ = 10.57 (s, 2H), 10.44 (s, 2H), 9.30 (d, 2H), 9.13 (d, 2H), 8.97 (m, 4H), 7.30 (m, 6H), 7.26 (m, 12H), 3.12 (b, 6H), 2.77 (m, 6H), 1.11 (m, 24H), 1.06 (m, 12H), 1.03 (m, 12H), 0.94 (m, 12H), 0.74 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, 298K): δ = 164.0, 163.8, 163.6, 163.1, 163.0, 134.9, 134.7, 133.8, 132.6, 131.7, 130.9, 130.7, 130.6, 129.8, 129.7, 129.5, 129.4, 129.2, 128.9, 128.3, 127.7, 127.6, 126.0, 125.0, 124.8, 124.6, 124.3, 124.2, 124.1, 123.4, 122.9, 122.6, 121.9, 120.5, 118.9, 30.5, 30.2, 29.7, 29.2, 29.1, 28.8, 25.3, 25.1, 24.7, 24.3, 24.2, 24.1, 23.8, 22.7, 19.2.

MALDI-TOF,CCA,tripbi-1-18,2007,11,15



MALDI-TOF,CCA,tripbi-1-18,2007,11,15

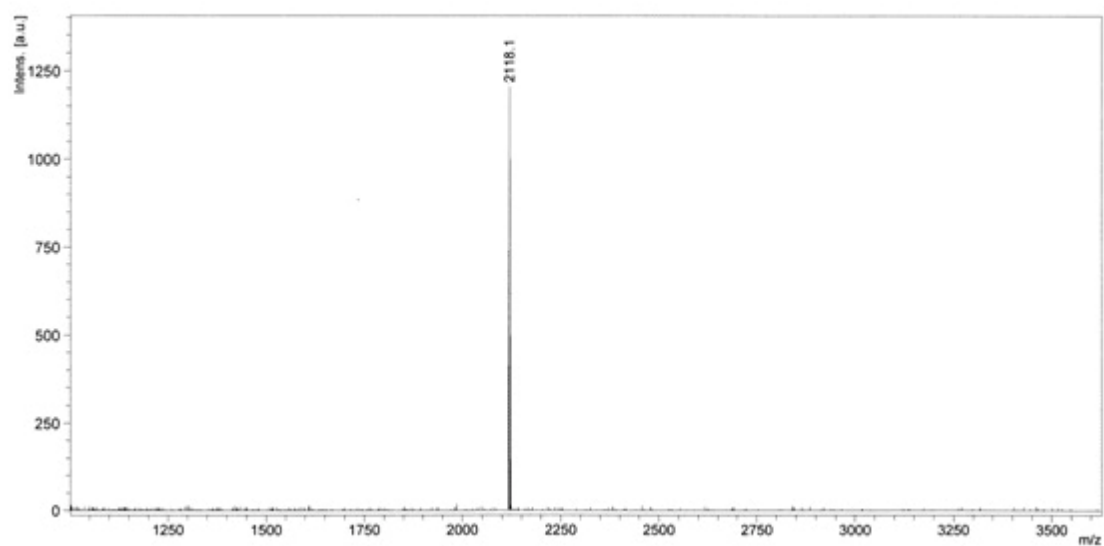
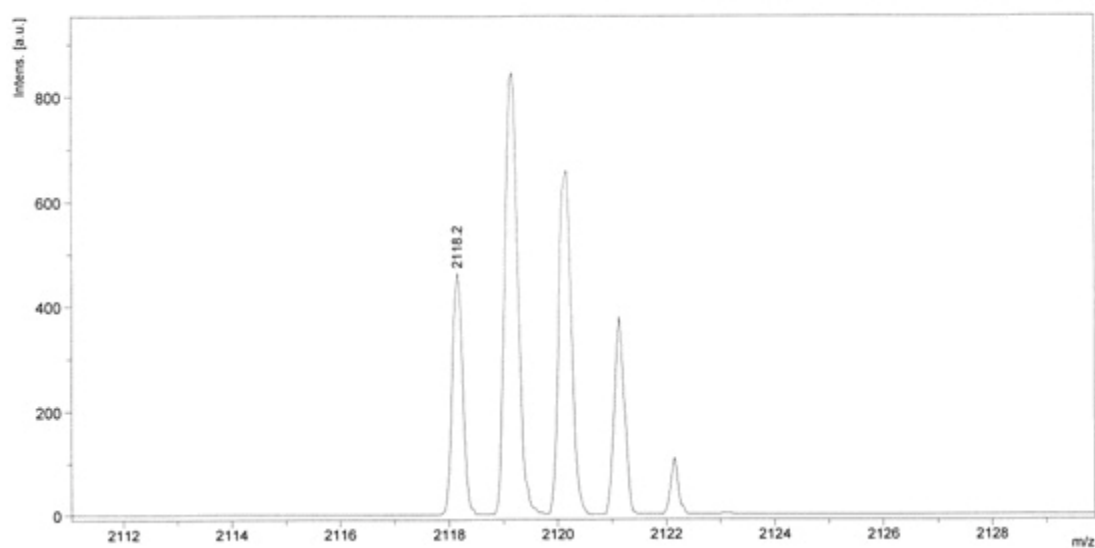


Figure S1: MALDI-TOF mass spectrum of tripBI 5.

MALDI-TOF,CCA,tripbi-2-27,2007,11,15



MALDI-TOF,CCA,tripbi-2-27,2007,11,15

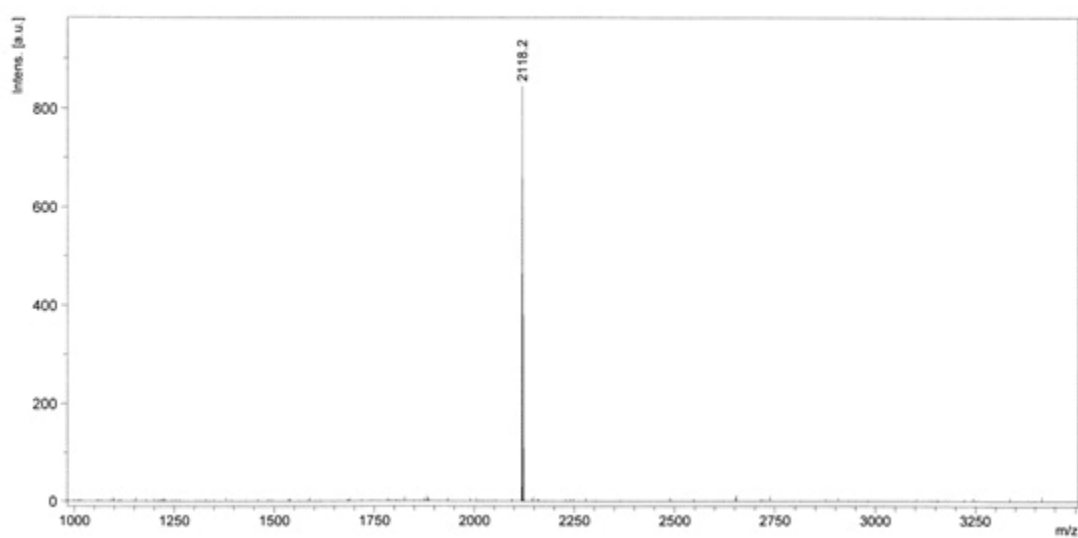


Figure S2: MALDI-TOF mass spectrum of triPBI 6.

References:

1. Qiu, W.; Chen, S.; Sun, X.; Liu, Y.; Zhu, D. *Org. Lett.* **2006**, *8*, 867-870.
2. (a) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551-554. (b) Sun, Q.; Wang, H.; Yang, C.; Li, Y. *J. Mater. Chem.* **2003**, *13*, 800-806.

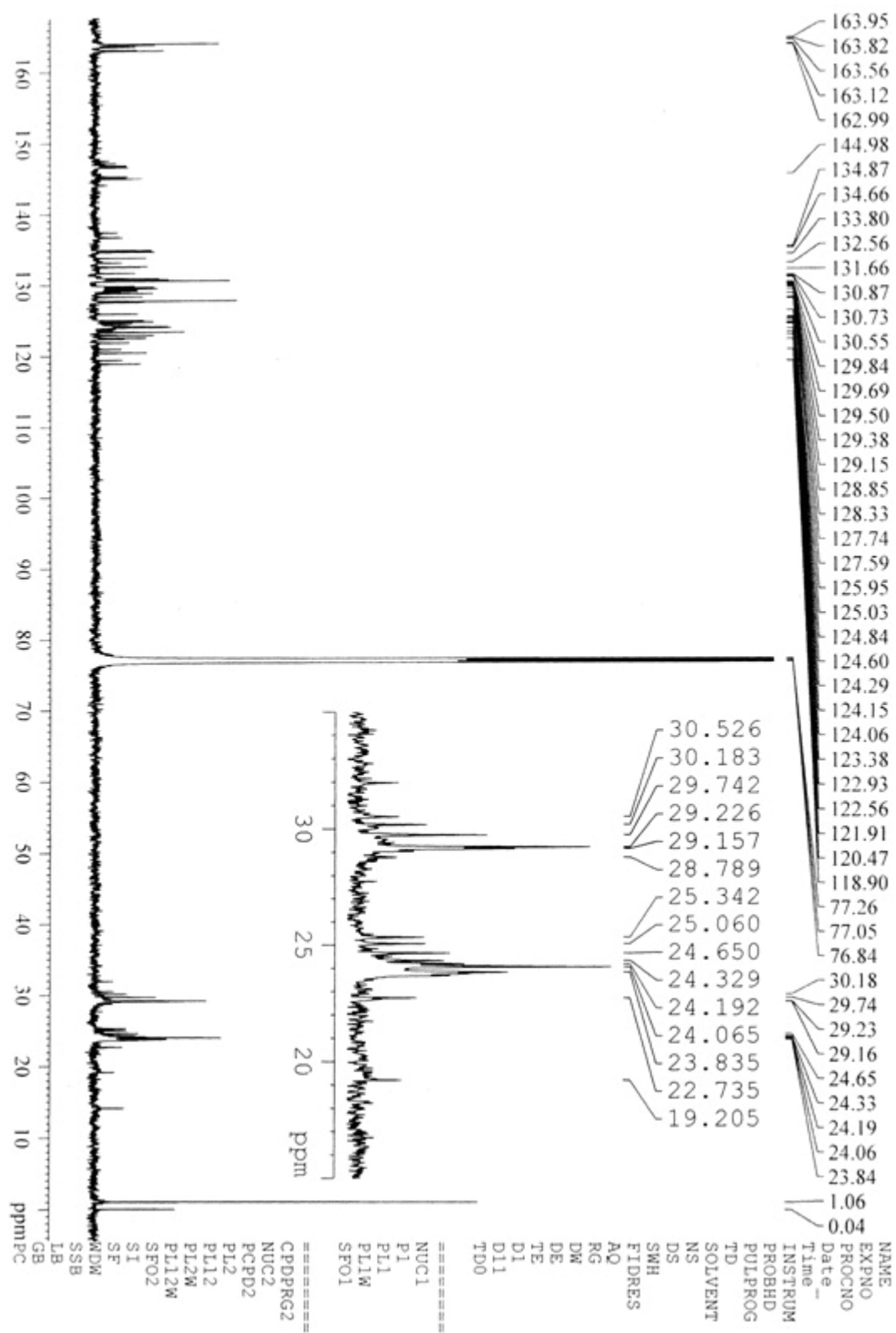
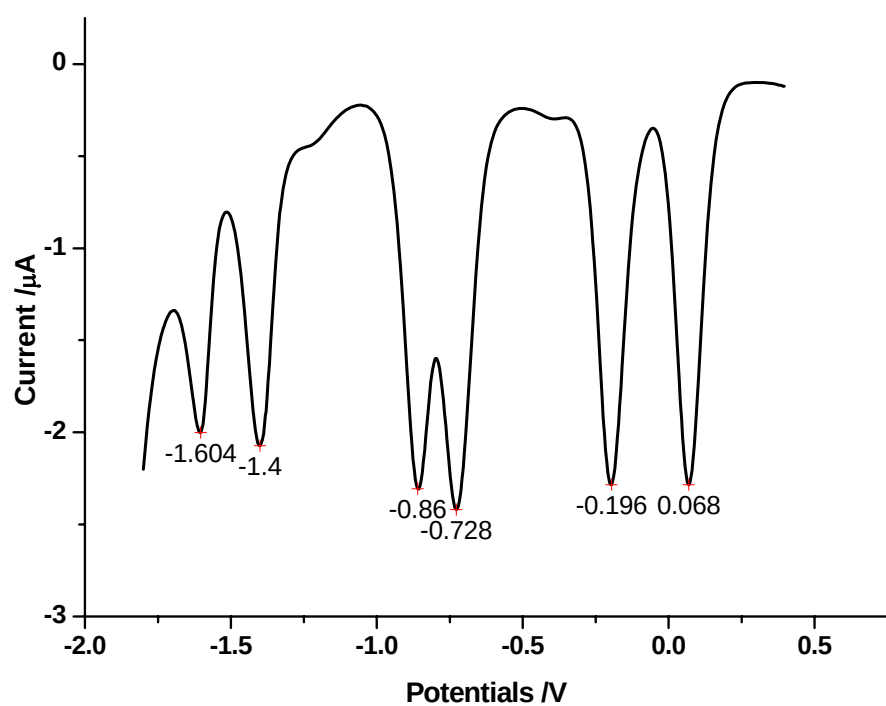
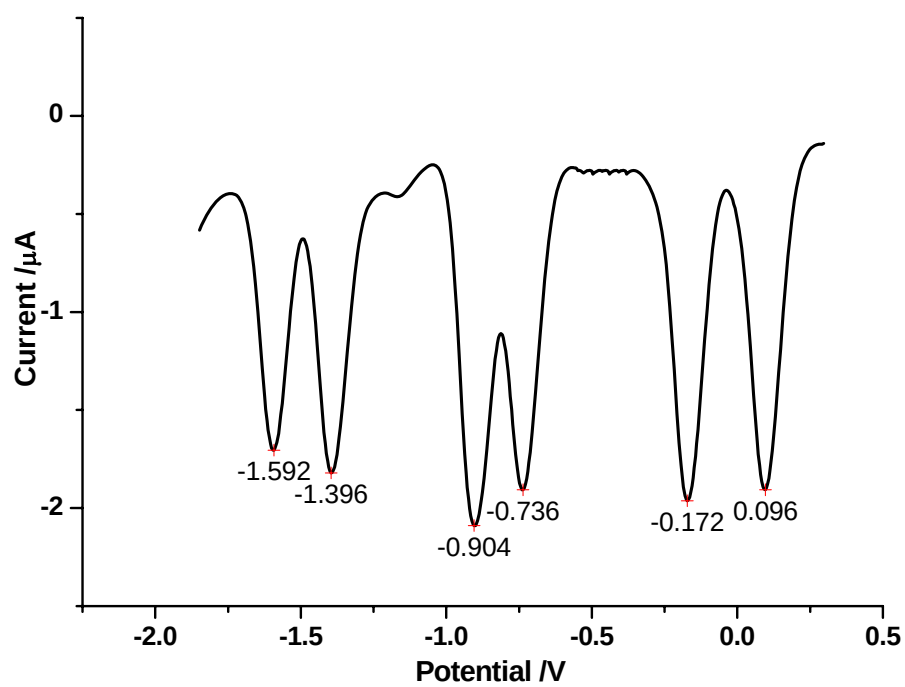


Figure S3: ^{13}C NMR of triPBI 6.

DPV of triPBIs 5 and 6:



(a)



(b)

Figure S4: Differential pulse voltammetry (in V vs Ag/AgCl) of triPBIs 5 (a) and 6 (b).

Computed structures, spectra and MO energies:



Figure S5: the B3LYP/3-21G computed structures of PBI 1.

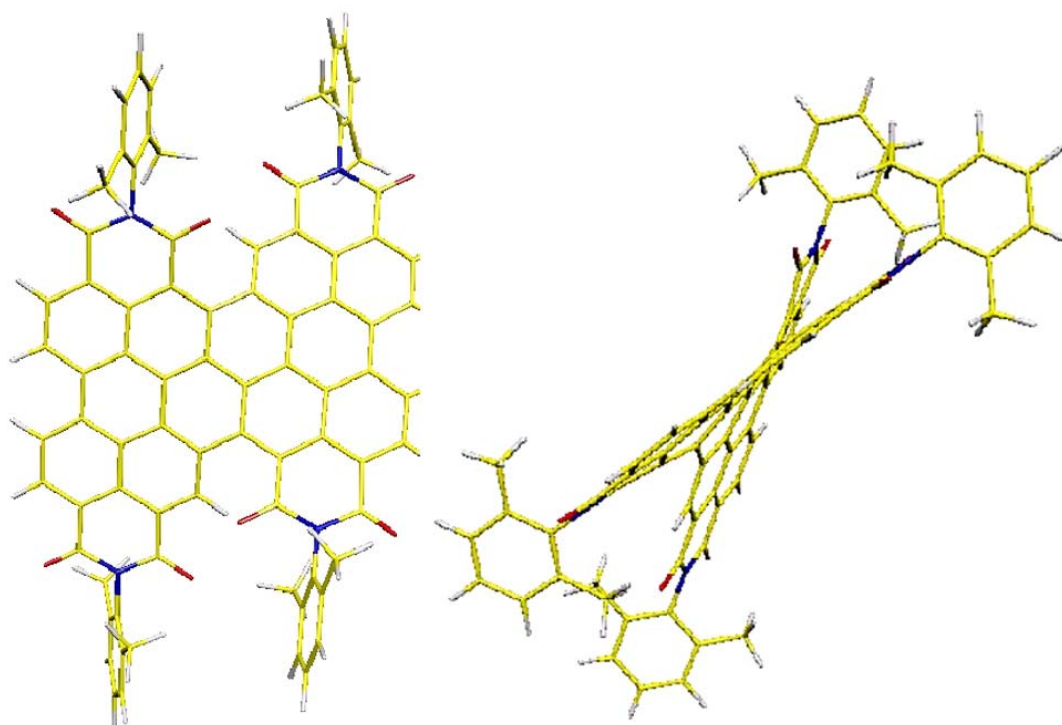


Figure S6: the B3LYP/3-21G computed structures of diPBI 4.

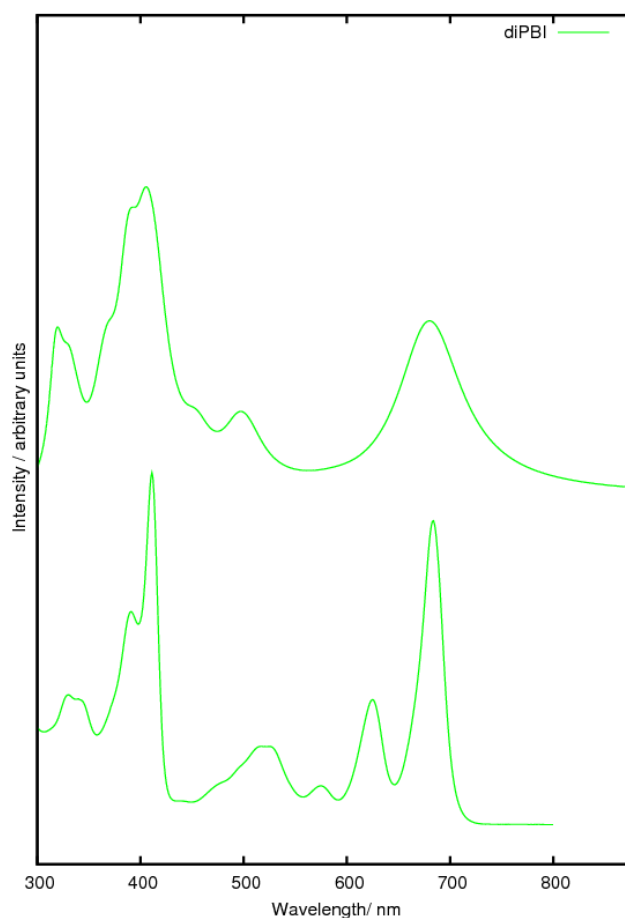


Figure S7. Top: the TDDFT calculated absorption spectrum of **4**; bottom: absorption spectrum of **4** in CHCl₃

Table S1: MO energies and HOMO-LUMO gaps of PBI, diPBI, and triPBIs. From B3LYP/3-21G calculations at optimized geometries

	HOMO (ev)	LUMO (ev)	LUMO+1 (ev)	LUMO+2 (ev)	E(H-L) (ev)
PBI 1	-6.14	-3.56	---	---	2.58
diPBI 4	-6.04	-4.06	-3.28	---	1.98
triPBI 5 ^a	-6.04 (-6.03)	-4.25 (-4.26)	-3.68 (-3.68)	-3.20 (-3.20)	1.79 (1.77)
triPBI 6 ^a	-6.00 (-5.99)	-4.29 (-4.30)	-3.69 (-3.68)	-3.20 (-3.19)	1.71 (1.69)

^ain parenthesis the values for non-helical isomer of triPBIs

Table S2: B3LYP/3-21G absolute energies, relative energies, optical gaps (lowest allowed electronic transitions from TDDFT B3LYP/3-21G calculations), and HOMO-LUMO gaps

	Absolute Energy (a.u.)	Relative Energy (kcal/mol)	E(S ₀ →S ₁) (eV, [nm]) and <i>f</i>	E(H-L) (eV)
5 -helical	-5812.07873469	0.00	1.63 [761] (0.28)	1.79
5 -non-helical	-5812.07865775	+0.05	1.61 [769] (0.30)	1.77
6 -helical	-5812.07601472	0.00	1.53 [811] (0.25)	1.71
6 -non-helical	-5812.07156895	+2.8	1.51 [822] (0.26)	1.69
4	-3875.90926192	0.00	1.82 [680] (0.39)	1.98

Full Citation of Reference 17.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc., Pittsburgh, PA, 2003.