

Supporting Information

Toward Electron-Deficient Pyrene Derivatives: Construction of Pyrene Tetracarboxylic Diimide Containing Five-Membered Imide Rings

Lin Zou,^a Xiao-Ye Wang,^a Xiao-Xiao Zhang,^b Ya-Zhong Dai,^a Yun-Dong Wu,^{*b} Jie-Yu Wang,^{**a} and Jian Pei^{*a}

^a Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.

^b Lab of Computational Chemistry and Drug Design, Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen 518055, P. R. China.

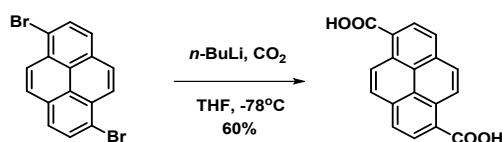
jianpei@pku.edu.cn, jieyuwang@pku.edu.cn, wuyd@pkusz.edu.cn.

Content:

1. Experimental Procedures
2. Computational Studies
3. Photophysical and Electrochemical Properties
4. Thermal Properties
5. Single-Crystal X-Ray Analysis
6. ¹H and ¹³C NMR Spectra

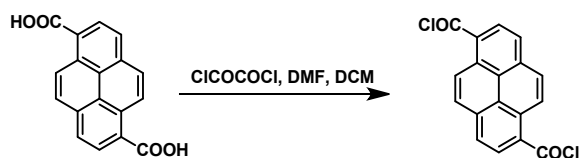
1. Experimental Procedures

General Methods. Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen atmosphere using the standard Schlenk method. Reagent grade tetrahydrofuran (THF) was distilled over sodium and benzophenone. Dichloromethane (DCM) was distilled over CaH₂ prior to use. Column chromatography was performed with silica gel. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica gel coated glass sheets with F254 indicator. Gel permeation chromatography (GPC) was performed on LC-9210NEXT using chloroform as eluent. NMR spectra were recorded on Bruker-400 (400 MHz) or Bruker-500 (500 MHz) using CDCl₃ as the solvent unless otherwise noted. All chemical shifts were reported in parts per million (ppm). ¹H NMR chemical shifts were referenced to TMS (0 ppm), and ¹³C NMR chemical shifts were referenced to CDCl₃ (77.00 ppm) or C₂D₂Cl₄ (73.78 ppm), respectively. High-resolution ESI FT mass spectra were recorded on a Bruker APEX IV mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer.



Pyrene-1,6-dicarboxylic acid (2)

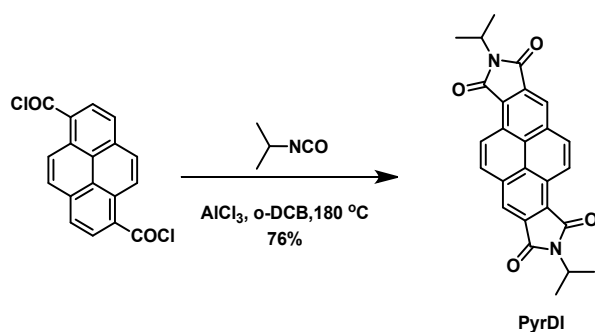
A 250 mL two-necked round-bottom flask was heated at 105 °C for 30 min and then cooled to room temperature. Then 1,6-dibromopyrene (3.6 g, 10 mmol) was added and the flask was degassed three times. 100 mL THF was added by syringe and the mixture was kept at -78 °C. *n*-BuLi (12.5 mL, 2.4 M, 30 mmol) was added into the solution dropwise in a period of 40 min at -78 °C. CO₂ gas was then bubbled into the solution continually at -78 °C for 30 min and then the mixture was kept at room temperature for another 20 min. After removing the solvent in vacuum, a yellow precipitate was obtained and then dissolved in 1000 mL of 5% NaOH aqueous solution. The solution was filtrated, and the filtrate was acidified with concentrated hydrochloric acid. The resulting precipitate was filtrated, washed with water and dried to afford the product as a dark-yellow solid (1.74 g, yield: 60%), which was used for next step without further purification. ¹H NMR (400 MHz, *d*₆-DMSO, 298 K, ppm): δ 13.49 (s, 2H), 9.31 (d, *J* = 9.4 Hz, 2H), 8.66 (d, *J* = 8.0 Hz, 2H), 8.46 (d, *J* = 8.1 Hz, 2H), 8.42 (d, *J* = 9.4 Hz, 2H). ¹³C NMR (100 MHz, *d*₆-DMSO, 298K, ppm): δ 168.9, 132.6, 129.9, 128.9, 128.7, 126.5, 125.9, 125.5, 123.6. HRMS (ESI): Calcd for C₁₈H₉O₄ [M - H]⁻: 289.0498; Found: 289.0495.



Pyrene-1,6-dicarbonyl dichloride (3)

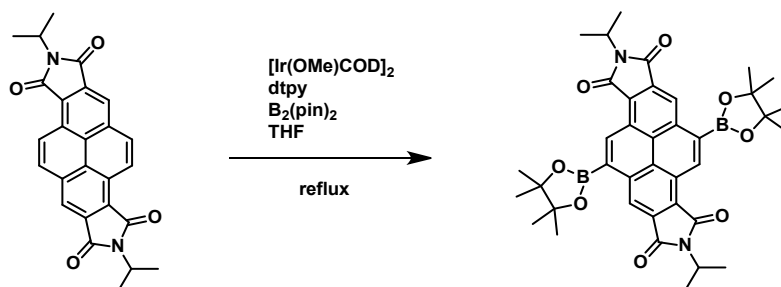
Dry DMF (3 drops) was added to a stirred suspension of pyrene-1,6-dicarboxylic acid (1.45 g, 5 mmol) and (COCl)₂ (7 mL, excess) in dry CH₂Cl₂ (100 mL) at 0 °C under argon atmosphere. After being stirred at room temperature for 24 h, the solvents were removed under reduced pressure to give the product as

a light yellow solid, which was used for next step without further purification.



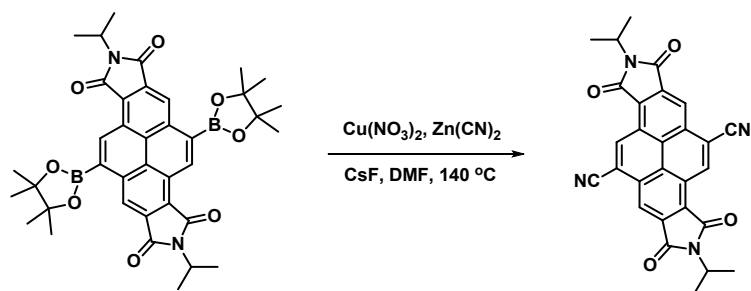
PyrDI (4)

Pyrene-1,6-dicarbonyl dichloride (200 mg, 0.62 mmol), AlCl_3 (491 mg, 3.69 mmol) and dry 1, 2-dichlorobenzene (9.0 mL) were charged into a Schlenk-flask under argon atmosphere, and the mixture was stirred for 5 min at room temperature. After *iso*-propyl isocyanate (1.05 g, 12.4 mmol) was added, the mixture was heated at 180 °C for 12 h. The residue was suspended in 150 mL CHCl_3 and filtrated over Celite. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography over silica gel (eluent: petroleum ether/DCM = 1:3) to afford **PyrDI** as a yellow solid (207 mg, yield: 78%). ^1H NMR (400 MHz, CDCl_3 , 298K, ppm): δ 9.37 (d, $J = 9.2$ Hz, 2H), 8.64 (s, 2H), 8.44 (d, $J = 9.2$ Hz, 2H), 4.72 (m, 2H), 1.62 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , 298K, ppm): δ 169.1, 168.2, 135.2, 131.9, 130.9, 128.2, 127.0, 125.8, 123.7, 120.4, 43.4, 20.3. HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{21}\text{N}_2\text{O}_4$ [$\text{M} + \text{H}$] $^+$: 425.1496; Found: 425.1496.



PyrDI-Bpin (6)

$[\text{Ir}(\text{OMe})\text{COD}]_2$ (63 mg, 0.094 mmol) and 4,4'-di-tert-butyl-2,2'-bipyridine (dtpy, 51 mg, 0.190 mmol), were dissolved in 20 mL THF under nitrogen atmosphere and refluxed for 1 h. Then $\text{B}_2(\text{pin})_2$ (723 mg, 2.52 mmol) dissolved in THF (5 mL) was added to the mixture and the mixture was refluxed for another 1 h. **PyrDI** (267 mg, 0.63 mmol) in 10 mL THF was added to the mixture, and the mixture was heated at 120 °C for 24 h. After cooled to room temperature, 30 mL CHCl_3 was added. The mixture was then filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was recrystallized from CHCl_3 and methanol to afford the product as a yellow solid. Further purification was performed by preparative recycling GPC to get the pure product (294 mg, yield: 69%) as a light yellow solid. ^1H NMR (400 MHz, CDCl_3 , 298K, ppm): δ 9.57 (s, 2H), 9.28 (s, 2H), 4.74 (m, 2H), 1.71 (d, $J = 6.8$ Hz, 12H), 1.57(s, 24H). ^{13}C NMR (100 MHz, CDCl_3 , 298K, ppm): δ 168.7, 168.5, 137.1, 135.4, 130.3, 126.8, 126.4, 123.1, 121.9, 84.8, 43.3, 25.0, 20.4. HRMS (ESI): Calcd for $\text{C}_{38}\text{H}_{43}\text{B}_2\text{N}_2\text{O}_8$ [$\text{M} + \text{H}$] $^+$: 677.3220; Found: 677.3212.



PyrDI-CN (7)

A Schlenk tube charged with **PyrDI-Bpin** (0.15 mmol, 100 mg), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.9 mmol, 218 mg), $\text{Zn}(\text{CN})_2$ (1.5 mmol, 175 mg), and CsF (0.6 mmol, 91 mg) was degassed for three times. After addition of DMF (20 mL), the tube was sealed under nitrogen atmosphere and heated at 140 °C for 36 h. After cooled to room temperature, the reaction mixture was filtrated and the filtrate was diluted with CHCl_3 , washed with water and dried over anhydrous Na_2SO_4 . After removal of solvents under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether/DCM = 1:6) to afford the product as a light yellow solid (30 mg, yield: 41%). ^1H NMR (400 MHz, $\text{C}_2\text{Cl}_4\text{D}_2$, 298K, ppm): δ 9.95 (s, 2H), 9.20 (s, 2H), 4.77 (m, $J = 6.9$ Hz, 2H), 1.64 (d, $J = 6.9$ Hz, 12H). ^{13}C NMR (125 MHz, $\text{C}_2\text{Cl}_4\text{D}_2$, 363K, ppm): δ 167.5, 166.3, 133.8, 132.6, 132.4, 127.3, 126.7, 125.8, 121.2, 115.7, 115.3, 44.5, 20.2. HRMS (ESI): Calcd for $\text{C}_{28}\text{H}_{19}\text{N}_4\text{O}_4$ $[\text{M} + \text{H}]^+$: 475.1412; Found: 475.1401.

2. Computational Studies

DFT calculations of frontier molecular orbital (FMO) were performed at the B3LYP/6-311G(d,p) level of theory with the Gaussian 09 software package¹. The cyclization mechanism were performed at the B3LYP/6-31G(d) level of theory.

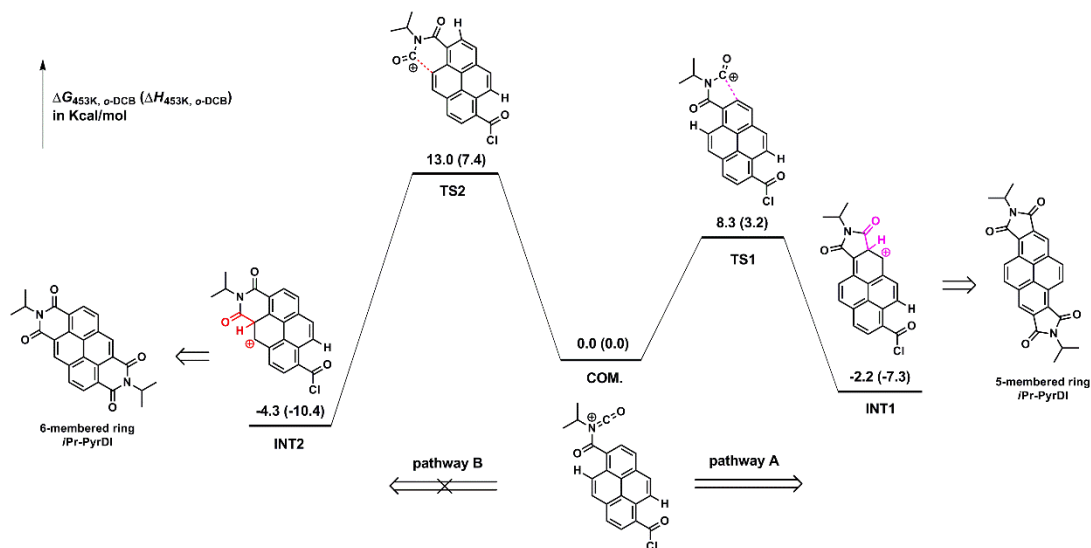


Figure. S1 DFT calculated free energy surface of the two competing pathways.

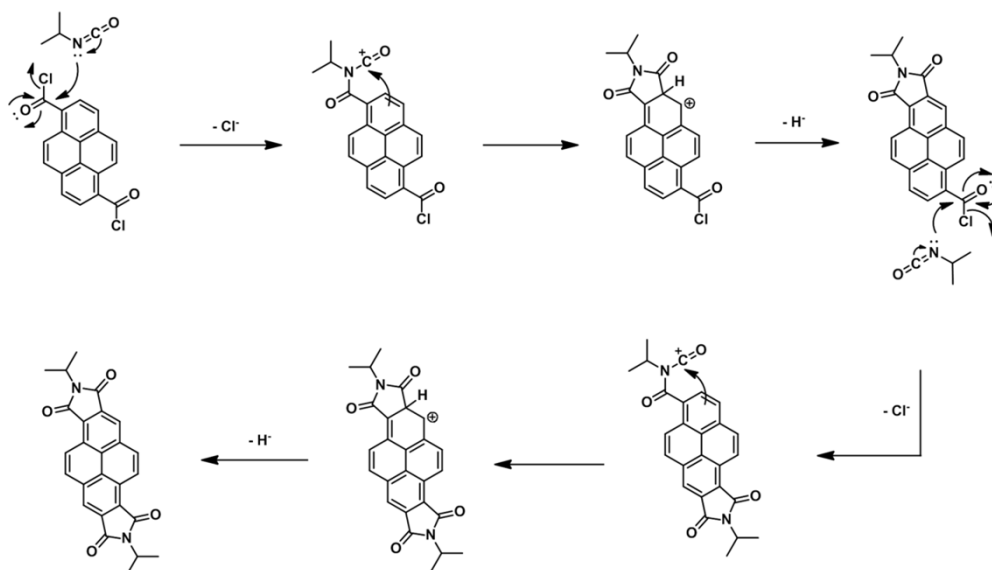


Figure S2. Proposed mechanism of the twofold cyclization (stepwise intramolecular cyclization). The catalyst (aluminium chloride) is omitted for clarity.

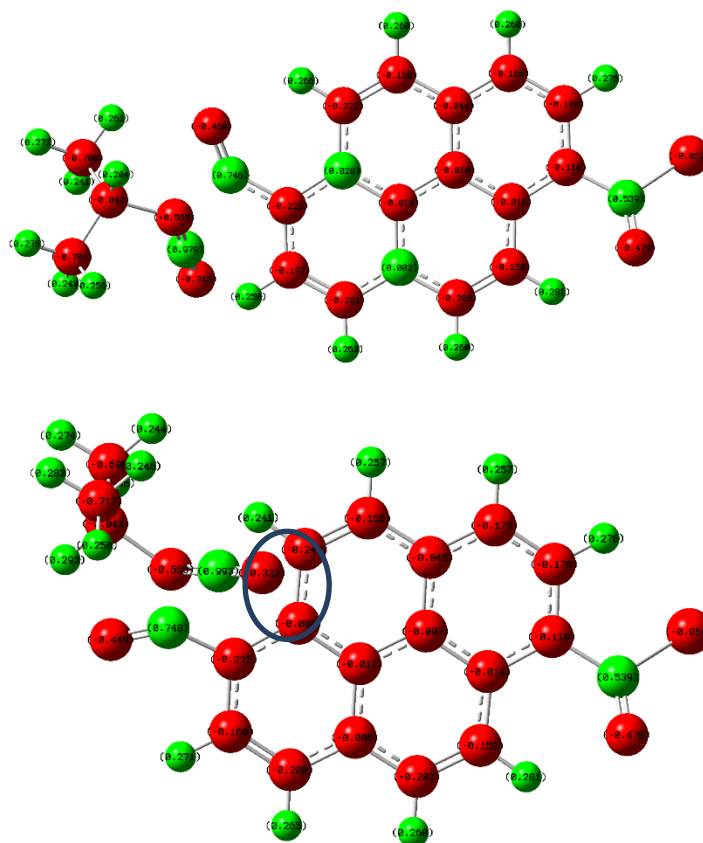


Figure S3. Charge distribution analysis of the formation pathway for the five-membered imide ring (upper), and that for the six-membered imide ring (lower) which shows negative charge repulsion.

[1] Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.

3. Photophysical and Electrochemical Properties

Absorption spectra were recorded on a PerkinElmer Lambda 750 UV-vis Spectrometer. Photoluminescence spectra were recorded on a EDINBURGH PHOTONICS FLS980 spectrofluorometer.

Steady-state fluorescence measurement was excited at 388 nm. Polystyrene ($M_w = 382100$) was dissolved in CHCl_3 (10 mg/mL), then **PyrDI** powder was added and stirred overnight at 60 °C. **PyrDI**/PS films were made by spin-casting. The neat film was casted from the saturated CHCl_3 solution of **PyrDI**. Cyclic voltammetry was performed on BASI Epsilon workstation and measurements were carried out in dichloromethane or acetonitrile containing 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte (scan rate: 50 mV s⁻¹). Glassy carbon electrode was used as working electrode, a platinum sheet as counter electrode and Ag/AgCl as reference electrode. All the potentials were calibrated with ferrocene as an external standard. The energy levels of the lowest unoccupied molecular orbitals (LUMO) of **PyrDI** and **PyrDI-CN** were calculated from the reductive onsets according to the following equation: $E_{\text{LUMO}} = - (4.8 + E_{\text{red}}^{\text{onset}})$ eV to be -3.44 and -3.86 eV. The HOMO energy levels were estimated from $E_{\text{HOMO}} = -E_{\text{g}}^{\text{opt}} + E_{\text{LUMO}}$ to be -6.17 and -6.69 eV, respectively.

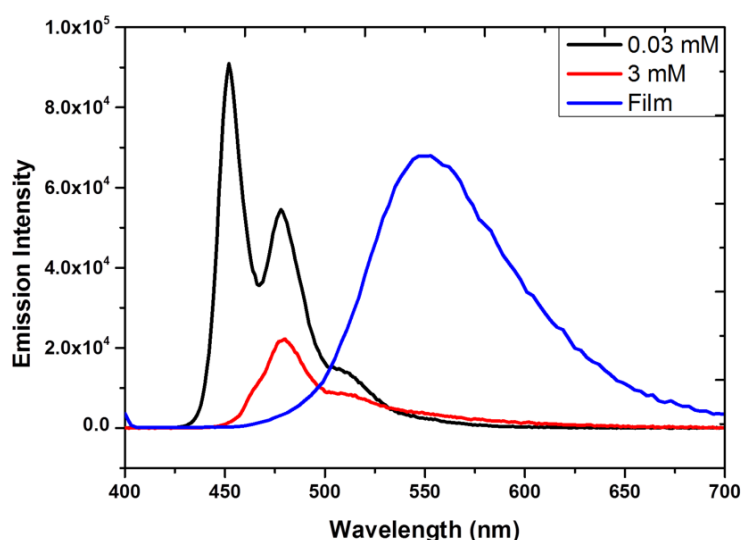


Figure S4. Emission spectra of **PyrDI** in 0.03 mM and 3 mM chloroform solution and in film state (excited at 388 nm).

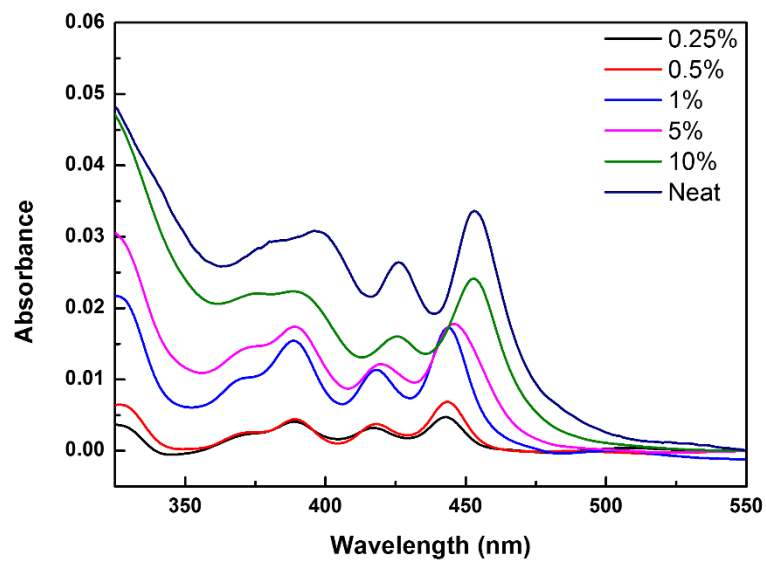


Figure S5. UV-vis absorption spectra of PyrDI in PS films upon varying the concentrations from 0.25 wt % to neat film.

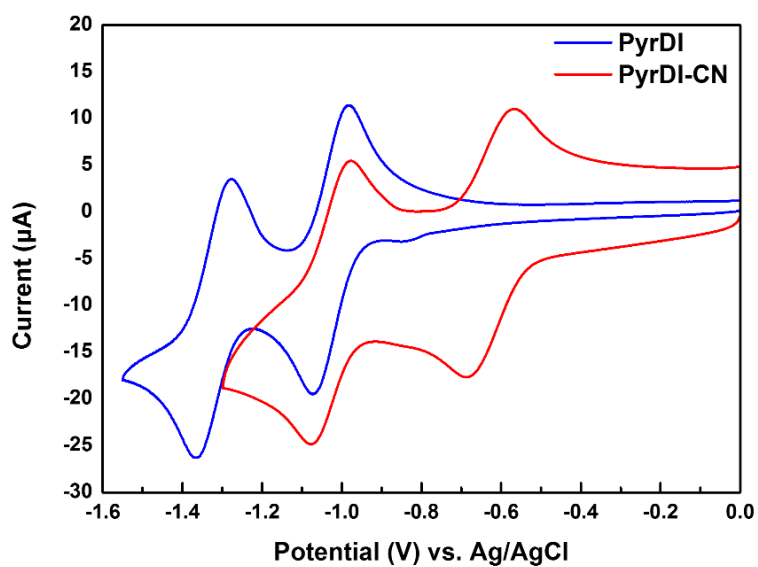


Figure S6. Cyclic voltammograms of PyrDI and PyrDI-CN in CH_2Cl_2 .

4. Thermal Properties

Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q600 analyzer under N₂ (10 °C min⁻¹). Differential scanning calorimetry (DSC) was performed on a METTLER TOLEDO Instrument DSC822e calorimeter under N₂.

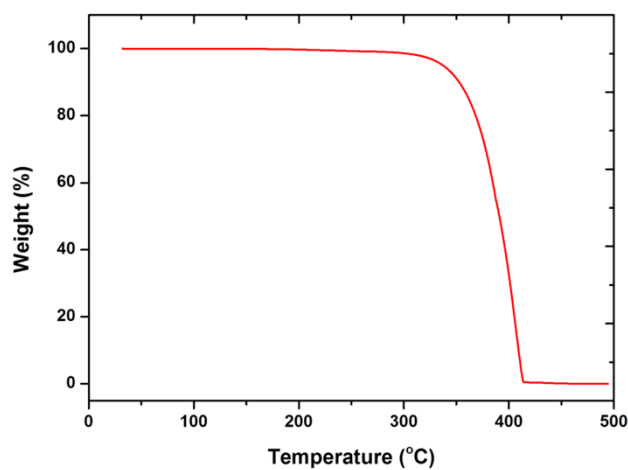


Figure S7. TGA trace of PyrDI (4) (5% weight loss: 337 °C).

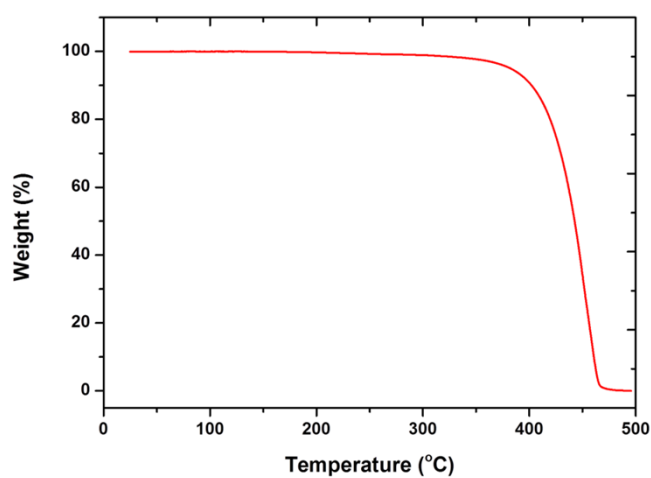


Figure S8. TGA trace of PyrDI-CN (7) (5% weight loss: 387 °C).

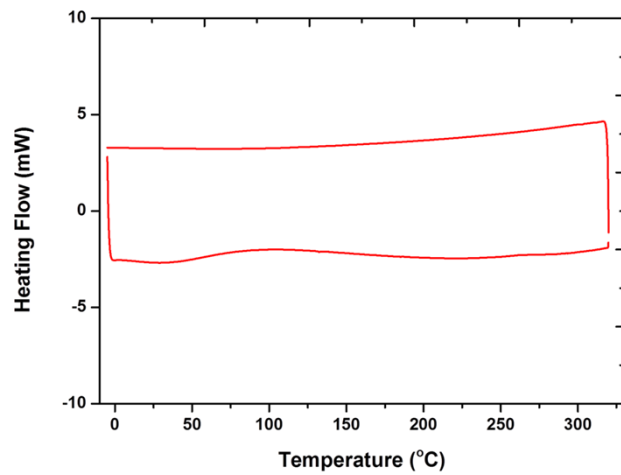


Figure S9. DSC trace of PyrDI (4).

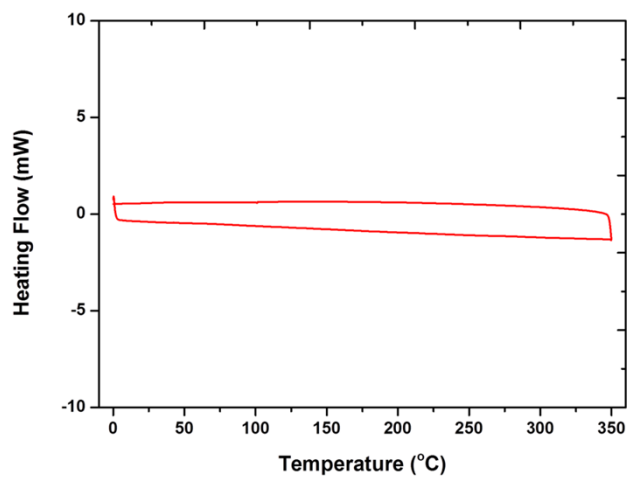


Figure S10. DSC trace of PyrDI-CN (7).

5. Single-Crystal X-Ray Analysis

Table S1. Crystal data and structure refinement for **PyrDI**. (CCDC: 1046692)

Empirical formula	C ₂₆ H ₂₀ N ₂ O ₄
Formula weight	424.44
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.3610(5)
b/Å	8.3907(5)
c/Å	16.3626(10)
α /°	80.826(5)
β /°	89.447(5)
γ /°	85.419(5)
Volume/Å ³	994.50(11)
Z	2
ρ_{calc} /mg/mm ³	1.417
m/mm ⁻¹	0.097
F(000)	444.0
Crystal size/mm ³	0.1 × 0.05 × 0.05
2 θ range for data collection	7.3 to 52.04°
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 8, -20 ≤ l ≤ 20
Reflections collected	6115
Independent reflections	3899[R(int) = 0.0149]
Data/restraints/parameters	3899/0/293
Goodness-of-fit on F ²	1.032
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0509, wR ₂ = 0.1253
Final R indexes [all data]	R ₁ = 0.0670, wR ₂ = 0.1363
Largest diff. peak/hole / e Å ⁻³	0.57/-0.27

6. ^1H and ^{13}C NMR Spectra

