Supplementary Information

Controlling the Photochromism of Zirconium Pyromellitic Diimide-Based Metal-Organic Frameworks through Coordinating Solvents

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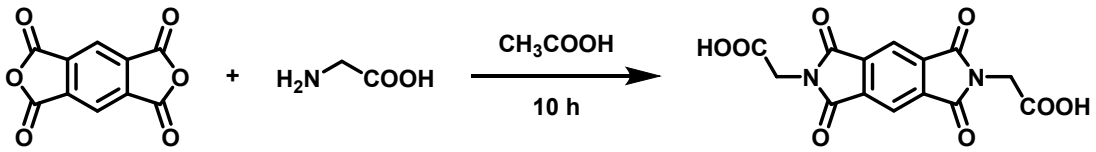
Materials and Instrumentation

All the reagents and solvents were commercially available and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Single-crystal X-ray diffraction intensity data for Zr-PMDI-DMF, Zr-PMDI-NMP, Zr-PMDI-DMSO, and Zr-PMDI-DMAE were collected on a Bruker D8 Venture diffractometer. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance III 400 NMR spectrometer. FT-IR spectra were recorded on a Vector 27 Bruker Spectrophotometer by transmission through KBr pellets containing the ground crystals in the range 4000 – 400 cm^{-1}. TGA data were obtained on a TGA 4000 thermal analysis system at a heating rate of 5 °C min^{-1} under an air atmosphere. The powder X-ray diffraction (PXRD) patterns were collected at room temperature using a scan speed of 0.1 s/step on a Bruker Advance D8 (40 kV, 40 mA) diffractometer equipped with Cu radiation. UV-vis absorbance spectra were recorded on Shimadzu UV-3600.

Experimental Section

Synthesis of H_2CMPMD

N,*N*′-bis(carboxymethyl)-pyromellitic diimide (H_2CMPMD) was synthesized according to the literature[1]. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) δ (ppm) 13.38 (s, 2H), 8.36 (s, 2H), 4.40 (s, 4H).



Scheme S1. Synthesis of H_2CMPMD.

Synthesis of Zr-PMDI-DMF

A mixture of H_2CMPMD (10 mg), $ZrOCl_2 \cdot 8H_2O$ (20 mg), and DMF (3 mL) is stirred for 10 min, and then the mixtures are placed in a 15 mL vial and heated at 120 °C for 36 h to yield colorless trigonal crystals. The crystals were collected by filtration and washed with fresh DMF three times (12.9 mg, yield: 82.0%).

Synthesis of Zr-PMDI-NMP

Crystals of compound Zr-PMDI-DMF (20 mg) were incubated in NMP (10 mL) at room temperature. The supernatant was replaced with fresh NMP (10 mL) every 6 h. After 48 h, the crystals were collected by filtration (12.7 mg, yield: 70.2 %).

Synthesis of Zr-PMDI-DMSO

Crystals of compound Zr-PMDI-DMF (20 mg) were incubated in DMSO (10 mL) at room temperature. The supernatant was replaced with fresh DMSO (10 mL) every 6 h. After 48 h, the crystals were collected by filtration (14.1 mg, yield: 78.82 %).

Synthesis of Zr-PMDI-DMAE

Crystals of compound Zr-PMDI-DMF (20 mg) were incubated in DMAE (10 mL) at room temperature. The supernatant was replaced with fresh DMAE (10 mL) every 6 h. After 48 h, the crystals were collected by filtration (14.5 mg, yield: 70.9 %).

Single Crystal X-Ray Crystallography

Single-crystal X-ray diffraction intensity data for Zr-PMDI-DMF, Zr-PMDI-NMP, Zr-PMDI-DMSO, and Zr-PMDI-DMAE were collected on a Bruker D8 Venture diffractometer fitted with a PHOTON-100 CMOS detector, monochromatized microfocus Mo Kα radiation (λ= 0.71073 Å), and a nitrogen flow controlled by a KRYOFLEX II low-temperature attachment operating at 193 K. Raw data collection and reduction were controlled using APEX3 software.[2] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[3]

DFT calculation for Zr-PMDI

For each solvent@MOF combination, 100 initial geometries were generated using the Kick stochastic structure generator. Positions of the solvent molecules were optimized using DFTB,[4, 5] keeping the framework fixed at the experimental geometry. The optimized structures were ranked in terms of energy and the energy levels of the HOMO and LUMO were extracted for the lowest energy structure of each solvent@MOF system.

To generate cube files for the frontier orbitals, single-point calculations of the DFTB-optimized geometry in periodic boundary conditions were performed at the DFT level. Density functional theory (DFT) was applied within the generalized gradient approximation, using the PBE GGA functional.

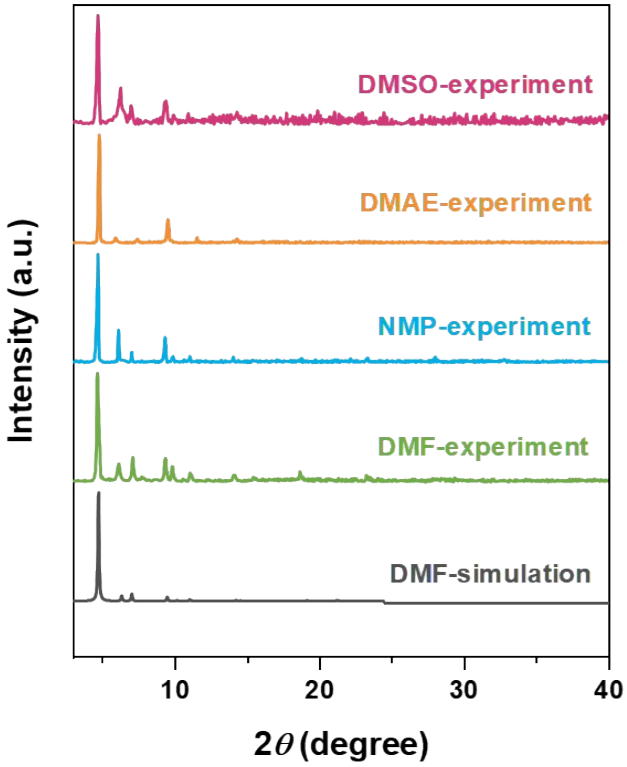
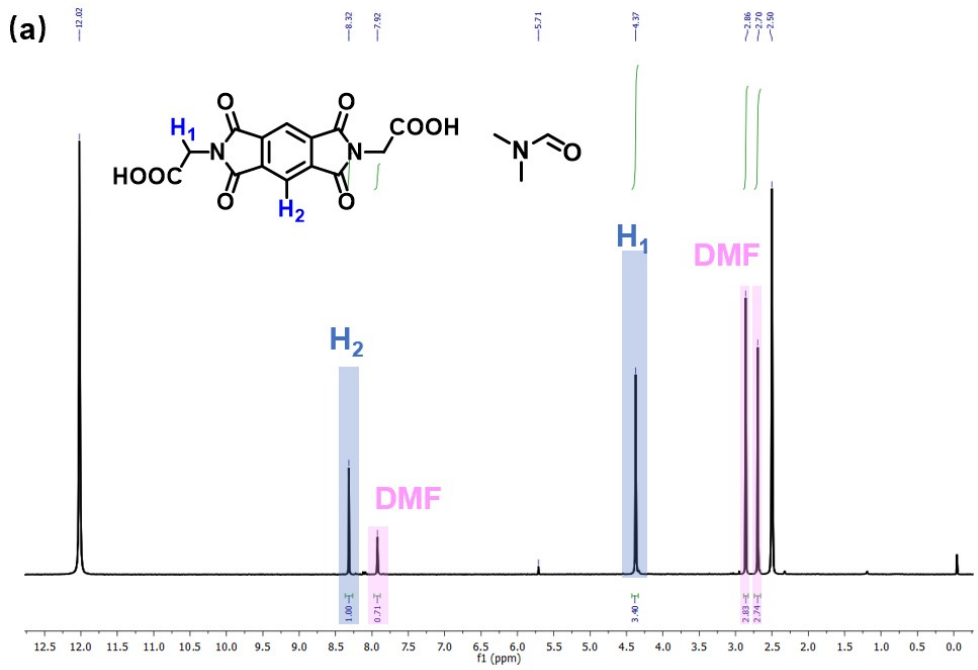
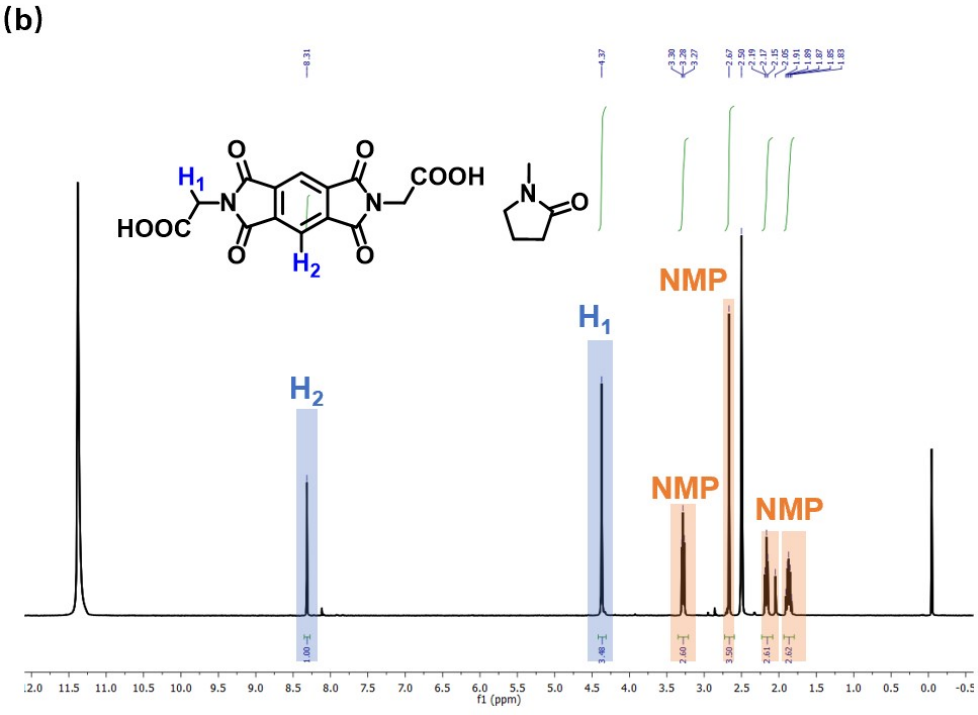


Figure S1. PXRD patterns of Zr-PMDI-DMF simulation from the X-ray single-crystal structures, as-synthesized sample, and the PXRD patterns of Zr-PMDI-DMF after soaking in NMP, DMAE, DMSO solution at room temperature for 48 h.


(a)
H1
H2
HOOC
COOH
DMF
DMF
f1 (ppm)


(b)
H1
H2
HOOC
COOH
NMP
NMP
NMP
f1 (ppm)

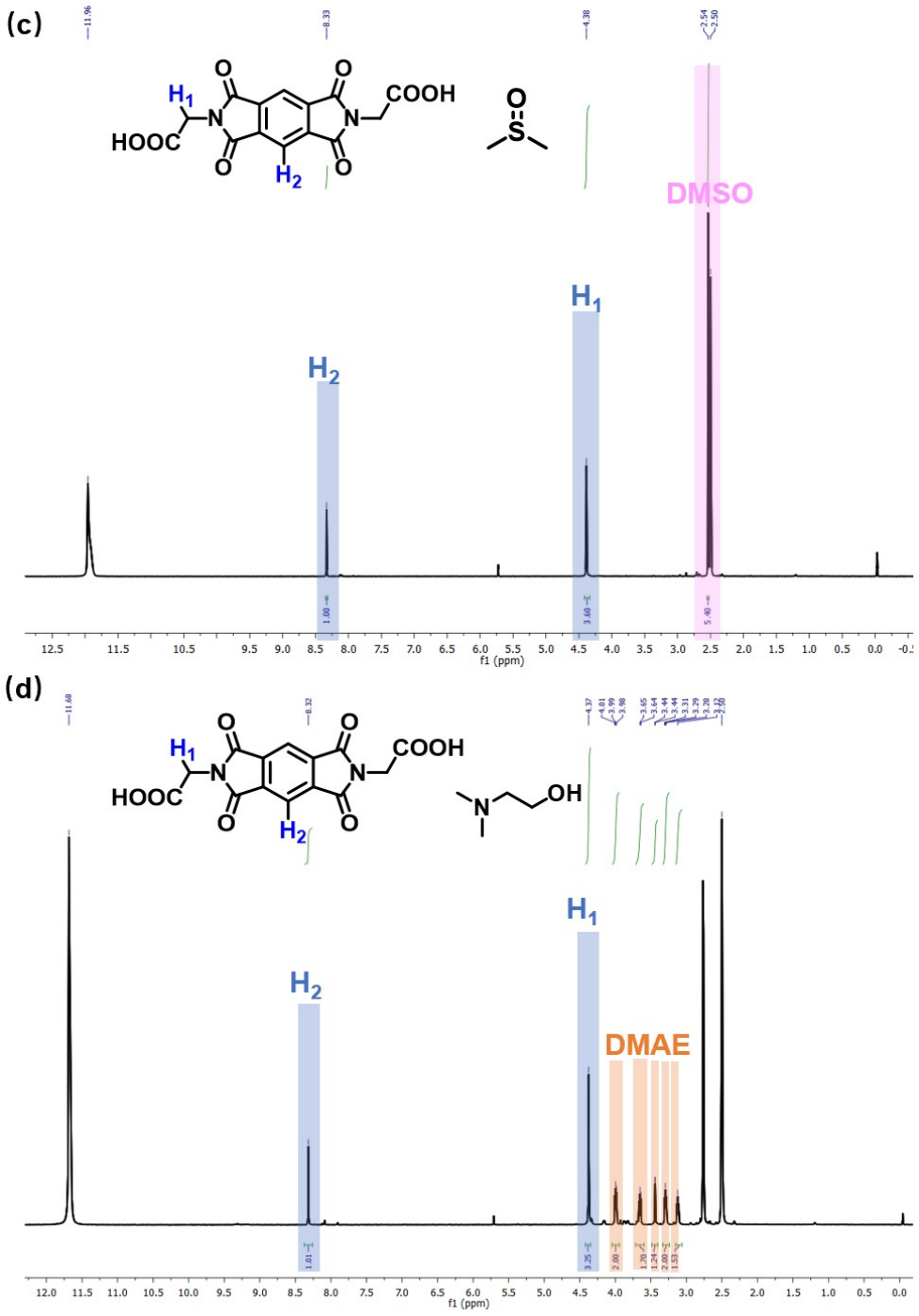


Figure S2. (a) ^{1}H-NMR spectrum of digested Zr-PMDI-DMF. (b) ^{1}H-NMR spectrum of digested Zr-PMDI-NMP showing complete conversion from Zr-PMDI-DMF to Zr-PMDI-NMP. (c) ^{1}H-NMR spectrum of digested Zr-PMDI-DMSO showing complete conversion from Zr-PMDI-DMF to Zr-PMDI-DMSO. (d) ^{1}H-NMR spectrum of digested Zr-PMDI-DMAE showing complete conversion from Zr-PMDI-DMF to Zr-PMDI-DMAE.

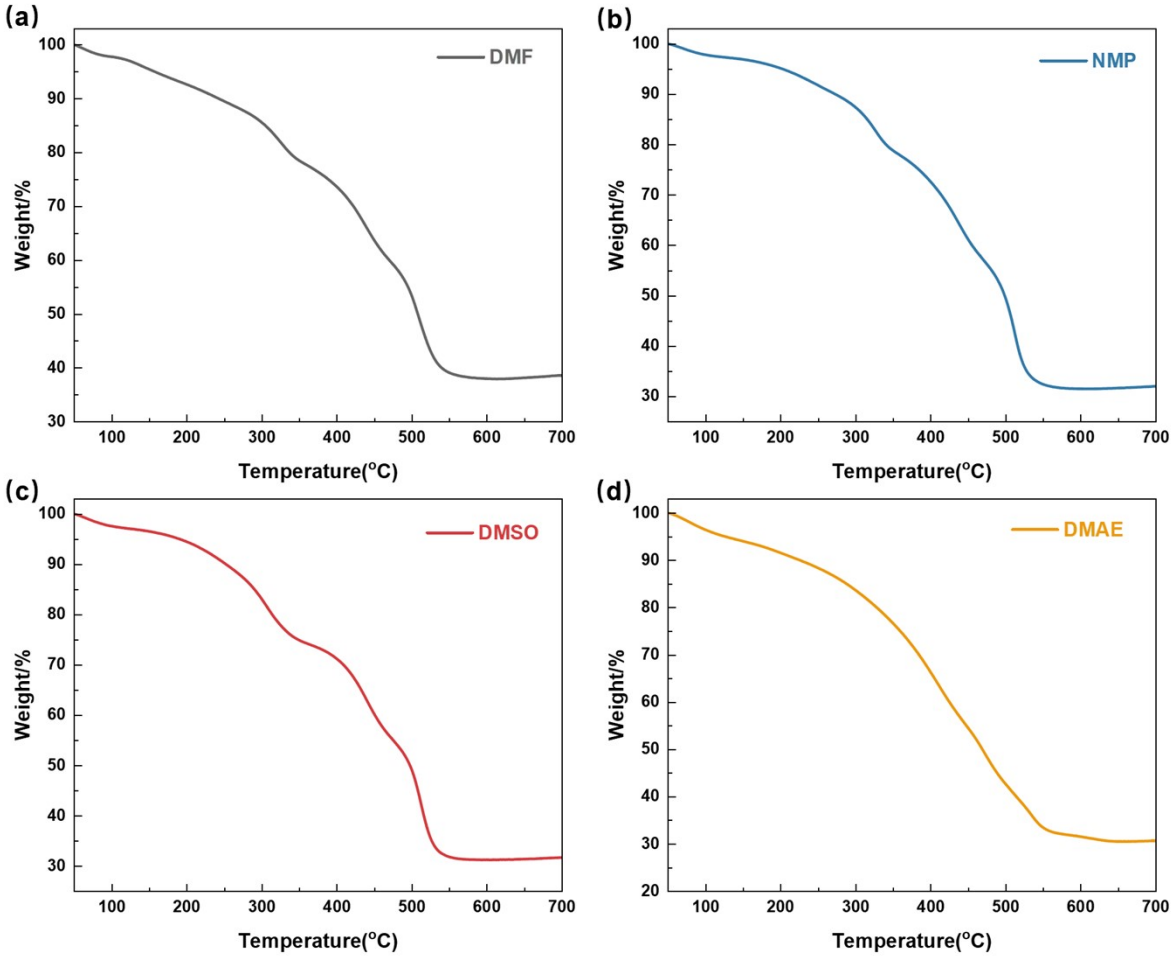


Figure S3. Thermo-gravimetric of Zr-PMDI-DMF (a), Zr-PMDI-NMP (b), Zr-PMDI-DMSO (c), and Zr-PMDI-DMAE (d).

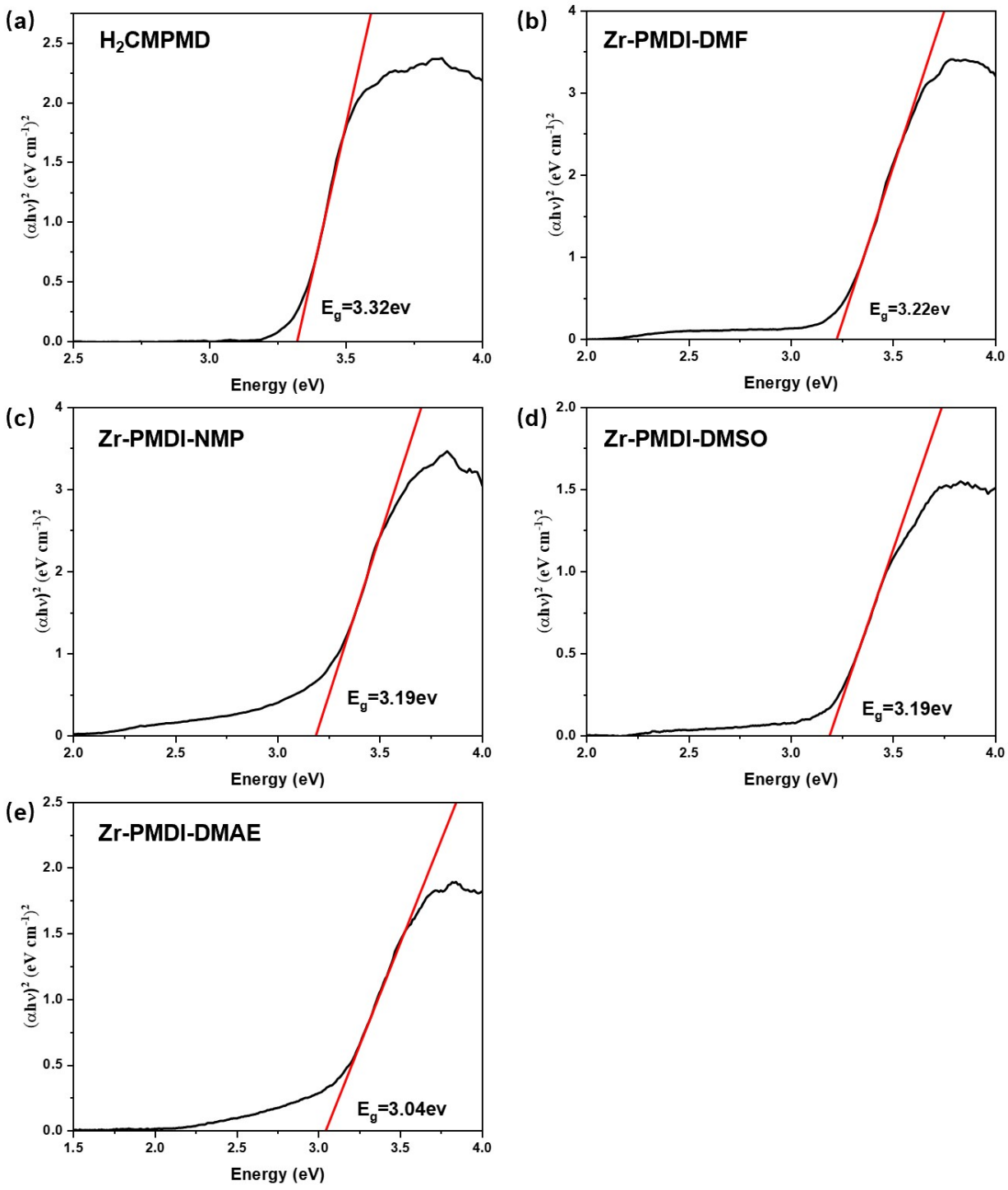


Figure S4. (a) The optical band gaps of H_2CMPMD; (b) The optical band gaps of Zr-PMDI-DMF; (c) The optical band gaps of Zr-PMDI-NMP; (d) The optical band gaps of Zr-PMDI-DMSO; (e) The optical band gaps of Zr-PMDI-DMAE.

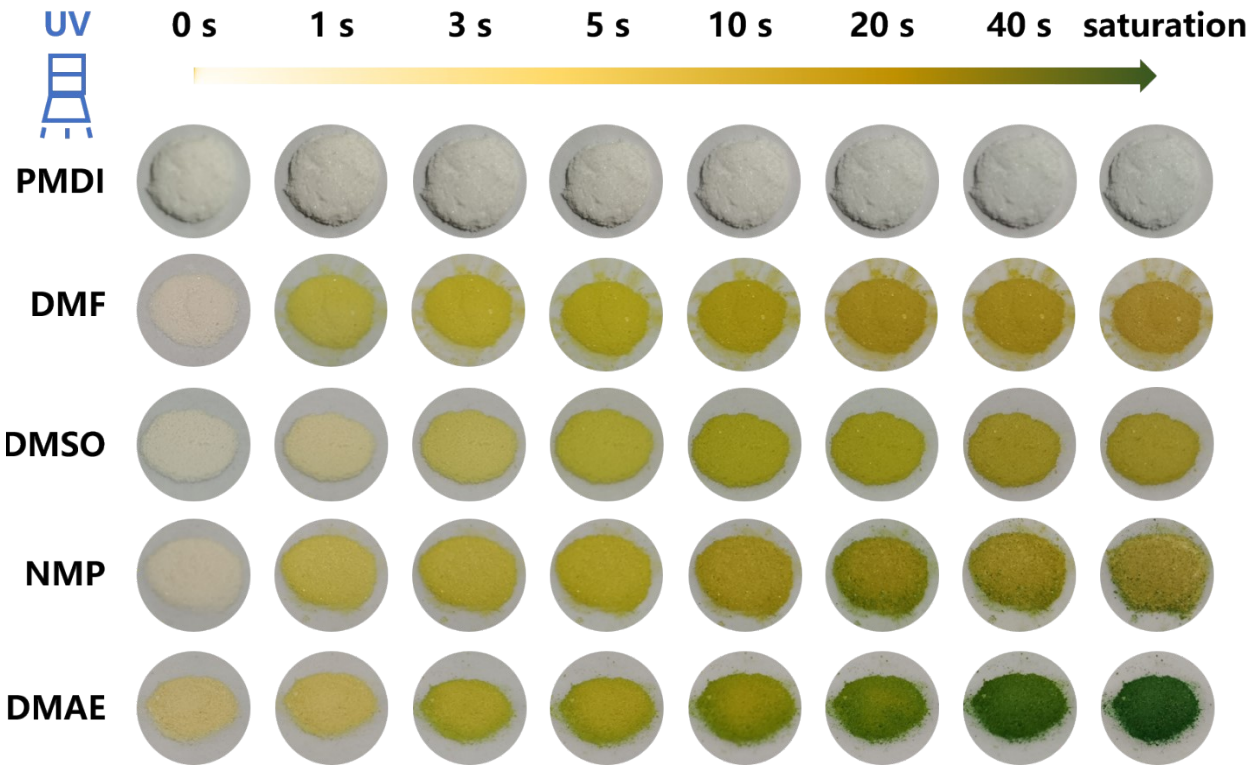


Figure S5. Photographs of the color transition process under a 365 nm UV light for PMDI, Zr-PMDI-DMF, Zr-PMDI-NMP, Zr-PMDI-DMSO, and Zr-PMDI-DMAE.

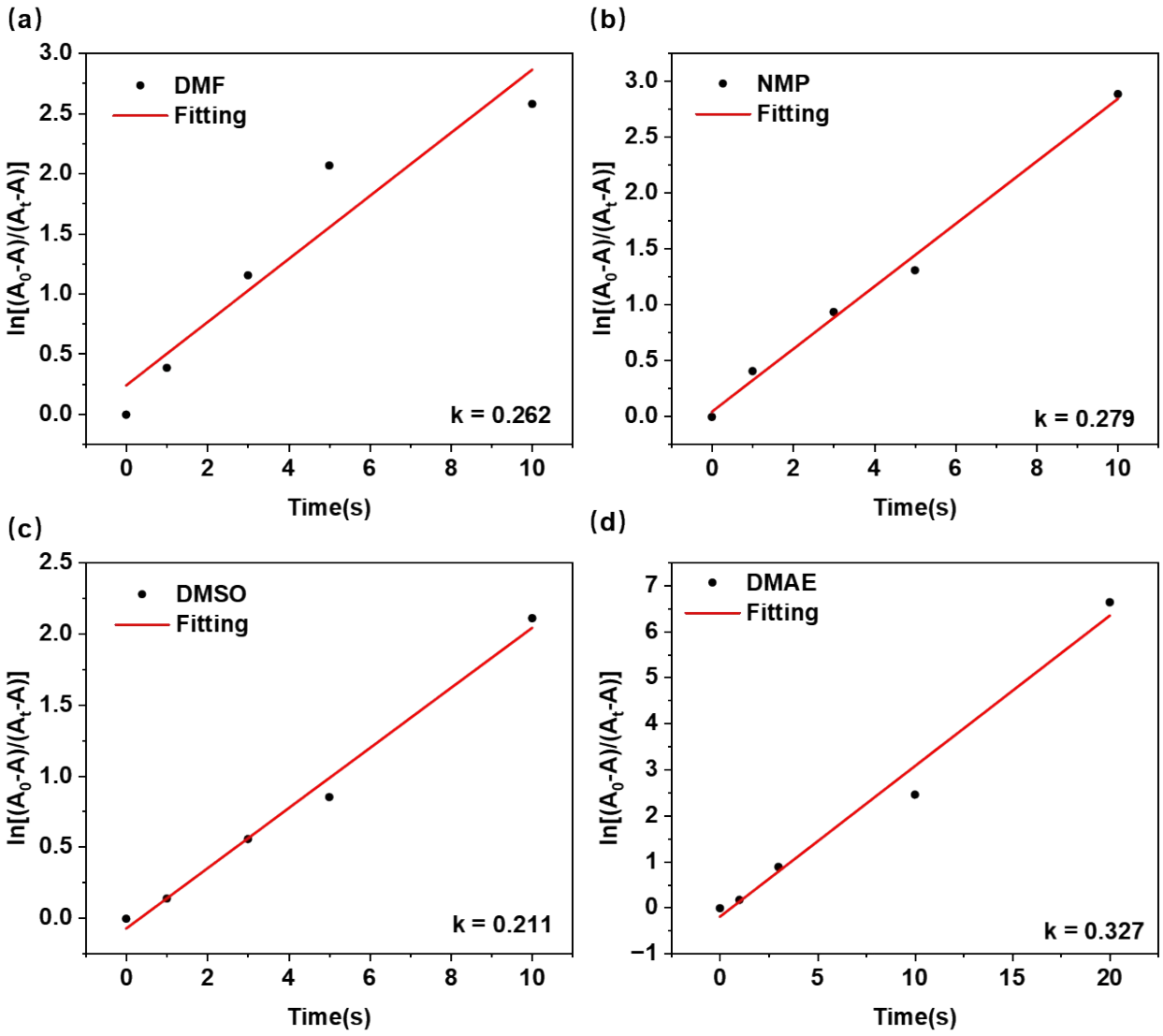


Figure S6. Kinetic curves for Zr-PMDI-DMF (a), Zr-PMDI-NMP (b), Zr-PMDI-DMSO (c), and Zr-PMDI-DMAE (d).

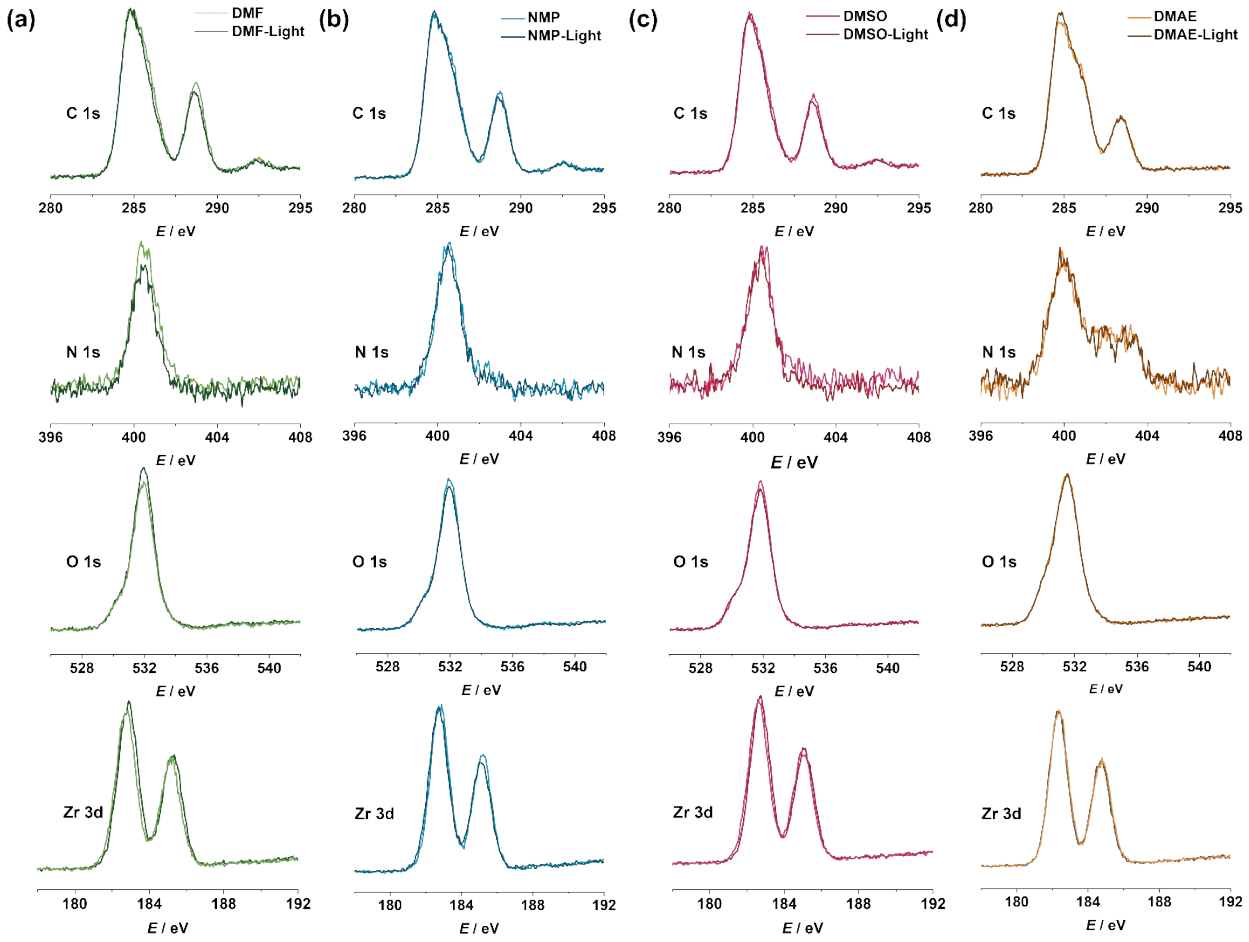


Figure S7. XPS spectra of Zr-PMDI-DMF and Zr-PMDI-DMF-Light (a), Zr-PMDI-NMP and Zr-PMDI-NMP-Light (b), Zr-PMDI-DMSO and Zr-PMDI-DMSO-Light (c), Zr-PMDI-DMAE and Zr-PMDI-DMAE-Light (d).

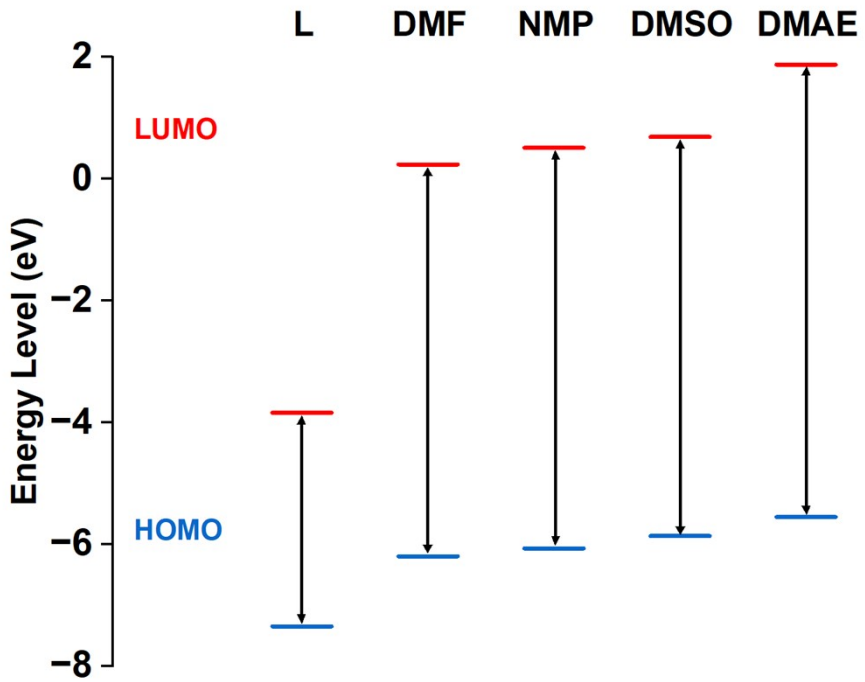


Figure S8. HOMO and LUMO energy levels of the PMDI ligand, DMF, NMP, DMSO, and DMAE.

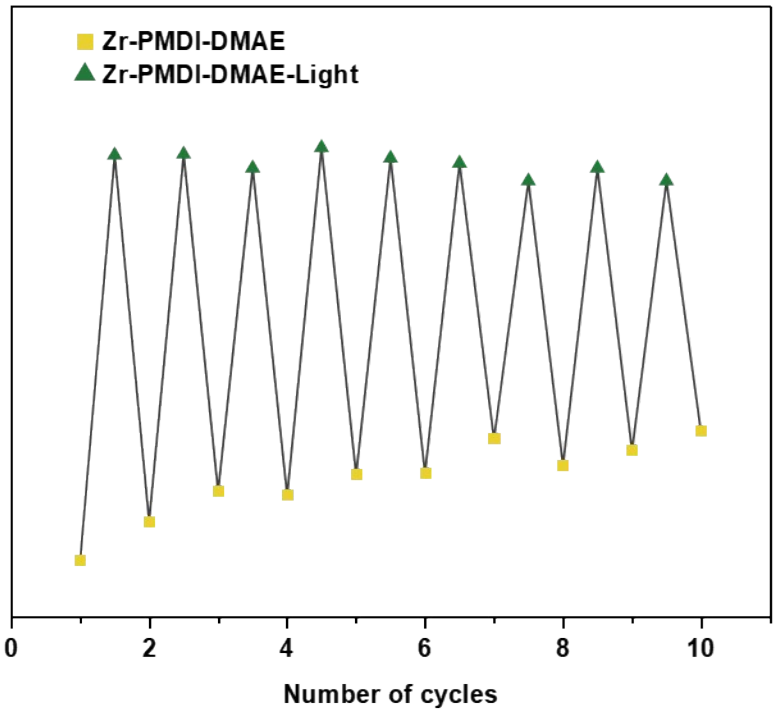


Figure S9. The repeated cycles of Zr-PMDI-DMAE and Zr-PMDI-DMAE-Light (based on absorbance at λ = 712 nm).

Single Crystal X-Ray Crystallography

Table S1 Crystal data and structure refinement parameters of Zr-PMDI-DMF, Zr-PMDI-NMP, and Zr-PMDI-DMSO.

Name	Zr-PMDI-DMF	Zr-PMDI-NMP	Zr-PMDI-DMSO
CCDC	2364996	2364997	2364998
Empirical formula	$C_{102}H_{84}N_{18}O_{63}Zr_6$	$C_{91.5}H_{53.5}N_{13.5}O_{58.5}Zr_6$	$C_{87}H_{51}N_{12}O_{58.5}S_{1.5}Zr_6$
Formula weight	3117.19	2825.29	2795.80
Temperature/K	193.00	193.00	193.00
Crystal system	trigonal	trigonal	trigonal
Space group	*R-3*	*R-3*	*R-3*
a/Å	27.698(4)	29.134(5)	29.323(4)
b/Å	27.698(4)	29.134(5)	29.323(4)
c/Å	29.419(6)	27.351(7)	27.527(6)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	120
V/Å^3	19546(7)	20105(8)	20499(7)
Z	3	3	3
ρ_{calc}/gcm^{-3}	0.794	0.700	0.679
μ/mm^{-1}	1.567	0.270	0.275
F(000)	4698.0	4215.0	4167.0
Crystal size/mm^3	0.12 × 0.1 × 0.08	0.12 × 0.1 × 0.08	0.12 × 0.1 × 0.08
Radiation	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)
2Θ range for data collection/°	5.552 to 107.806	4.844 to 51.232	4.44 to 50.88
Index ranges	$-33 \le h \le 30$, $-33 \le k \le 33$, $-30 \le l \le 35$	$-35 \le h \le 32$, $-35 \le k \le 35$, $-33 \le l \le 33$	$-35 \le h \le 35$, $-35 \le k \le 35$, $-33 \le l \le 33$
Reflections collected	46385	140447	129121
Independent reflections	7957 [R_{int} = 0.1034, R_{sigma} = 0.0696]	8346 [R_{int} = 0.1630, R_{sigma} = 0.0637]	8419 [R_{int} = 0.1781, R_{sigma} = 0.0584]
Data/restraints/parameters	7957/16/289	8346/149/332	8419/495/7345
Goodness-of-fit on F^2	0.910	1.057	1.143
Final *R* indexes [I>=2σ(I)][a,b]	R_1 = 0.0924, wR_2 = 0.2732	R_1 = 0.0984, wR_2 = 0.2762	R_1 = 0.1175, wR_2 = 0.3087
Final *R* indexes [all data][a,b]	R_1 = 0.1338, wR_2 = 0.3208	R_1 = 0.1323, wR_2 = 0.3122	R_1 = 0.1539, wR_2 = 0.3383
Largest diff. peak/hole / e Å^{-3}	0.95/-0.79	1.71/-1.17	2.09/-1.47

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

Table S2 Theoretical calculation of the energy levels of Crystal data and structure refinement parameters of the PMDI ligand, DMF, NMP, DMSO, and DMAE.

compound	HOMO (eV)	LUMO (eV)
PMDI	-7.346	-3.839
DMF	-6.197	0.237
NMP	-6.067	0.511
DMSO	-5.862	0.689
DMAE	-5.552	1.875

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(4) Aradi, B.; Hourahine, B.; Frauenheim, T. DFTB+, a Sparse Matrix-Based Implementation of the DFTB Method. *The Journal of Physical Chemistry A* **2007**, *111*(26), 5678-5684.

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