Electronic Supplementary Information

Persistent radical anion derived from a propeller-shaped perylene bisimide-carbazole pentad

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1. General experimental information

Solvents and reagents: All the solvents and reagents with at least analytical grade were purchased from commercial sources (Adamas-beta) and used as received without further purification. Cobaltocene ($CoCp_2$) was handled and stored in a glovebox.

Instrumental methods: Single-crystal X-ray diffraction was obtained using a Bruker SMART APEX II single-crystal X-ray diffraction spectrometer. UV-Vis-NIR absorption spectra in solution were recorded on a Perkin-Elmer Lambd 1050 spectrophotometer at room temperature. Electron paramagnetic resonance (EPR) measurements were carried out at room temperature using a Bruker ELEXSYS E500 EPR spectrometer. All samples were reduced using $CoCp_2$ as the chemical reductant and loaded into 1.4 mm I.D. quartz tubes, which were sealed with epoxy resin in an argon-filled glovebox and used immediately after preparation. Scans were performed with magnetic field modulation amplitude of 0.1 G. The optical images depicted in the paper were recorded using a Canon 70D camera. The light irradiation tests were carried out by white light of a xenon lamp from Beijing Perfectlight Technology Co., Ltd.

Quantum chemical calculation: The geometry of radical anion of PBI-4Cz was optimized by using the broken symmetry and the calculation was carried out using the DFT method with UCAM-B3LYP employing the 6-31G(d) basis set for all atoms. The calculated results were processed by Multiwfn.[1-3]

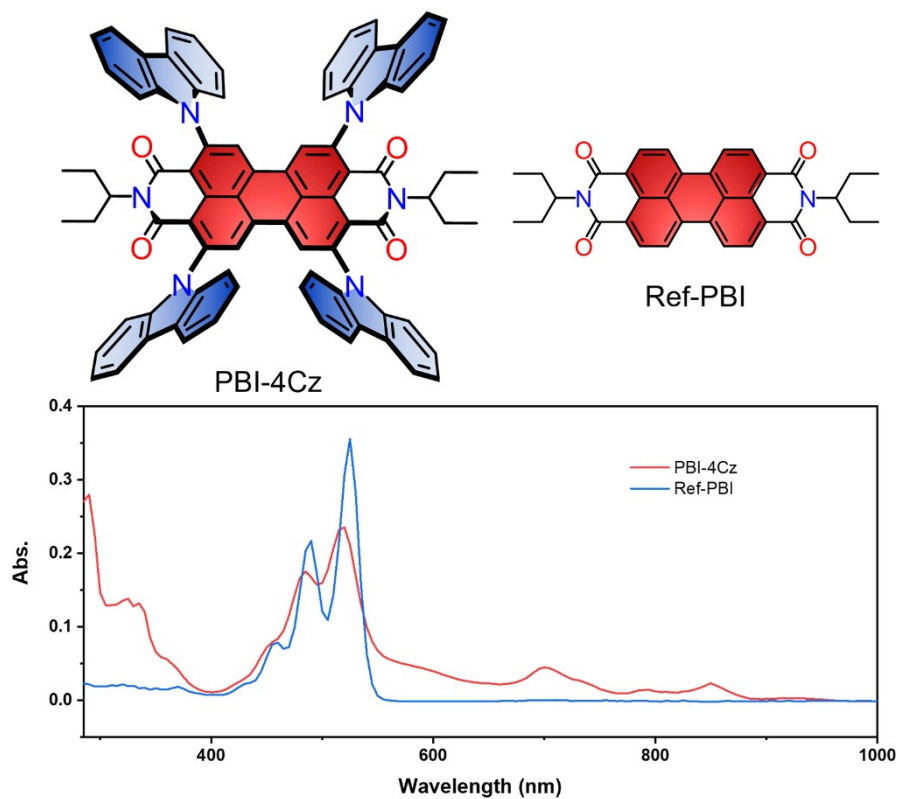## 2. Supplementary figures and tables

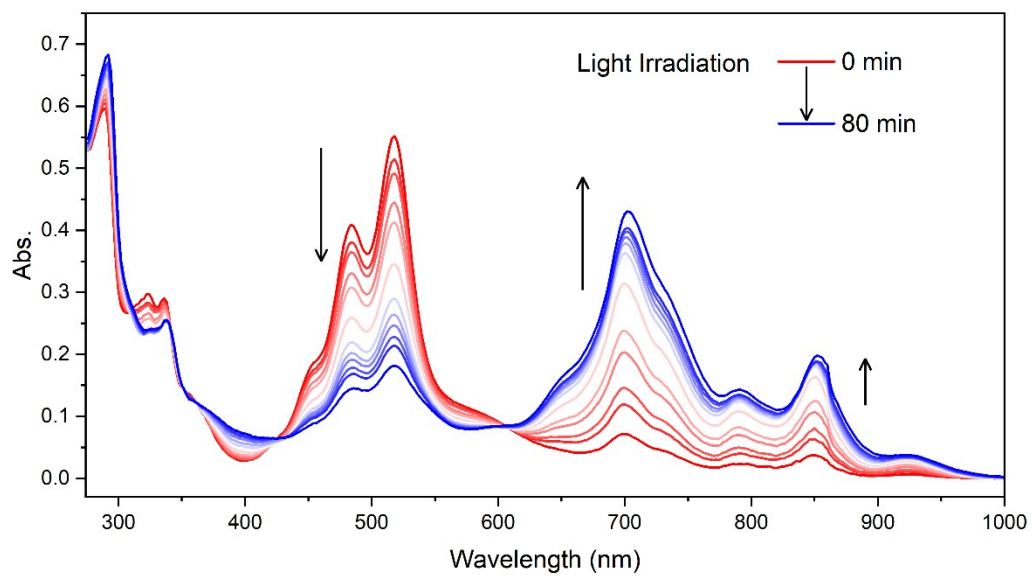**Figure S1.** Chemical structures of PBI-4Cz and Ref-PBI and their UV-Vis-NIR absorption spectra in DMF.

Figure S2. Changes in the UV-Vis-NIR absorption spectra of PBI-4Cz in DMF upon light irradiation ($C\sim 1.0 \times 10^{-5}$ mol/L).
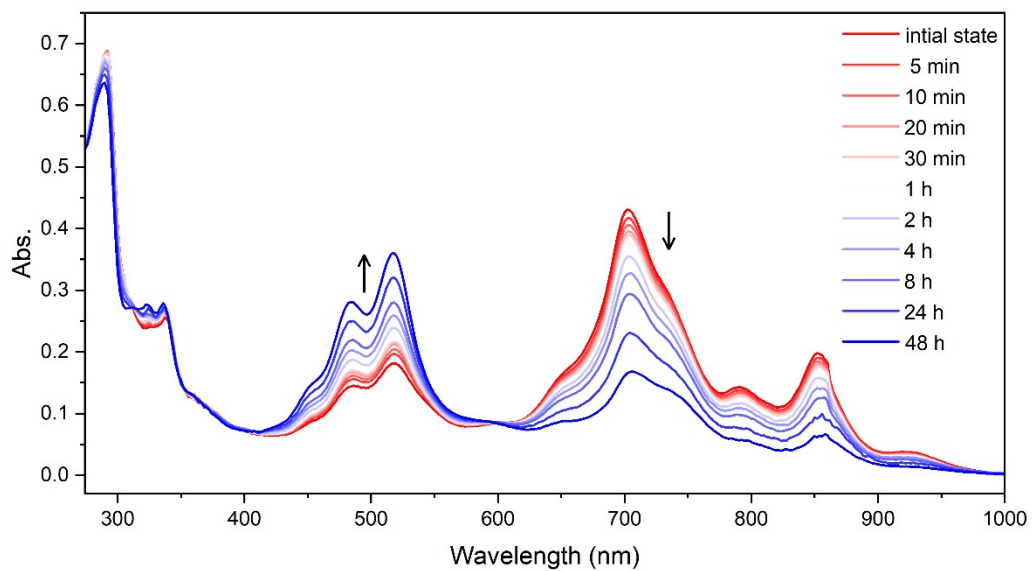
Figure S3. Time-dependent UV-Vis-NIR spectra of PBI-4Cz in DMF under dark condition ($C\sim 1.0 \times 10^{-5}$ mol/L).
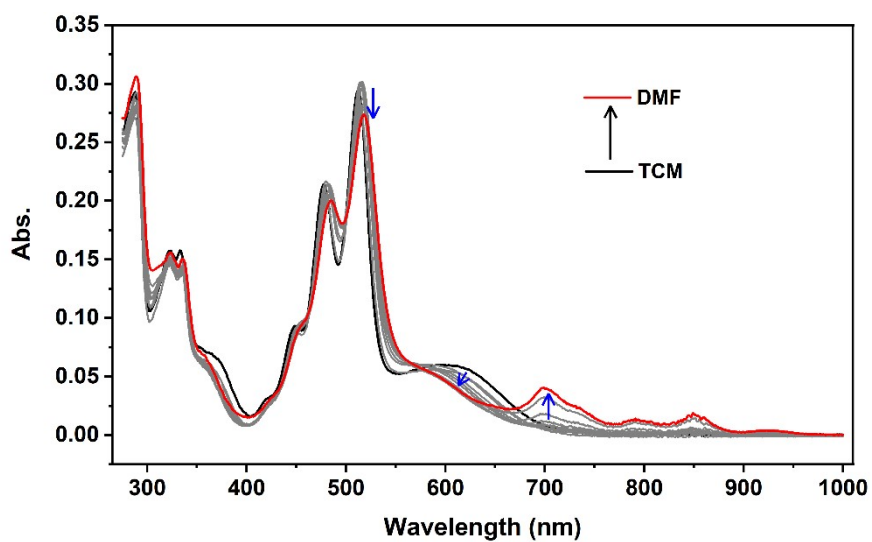
Figure S4. UV-Vis-NIR absorption spectra of PBI-4Cz in the binary mixture of DMF and chloroform ($C\sim 5.0 \times 10^{-6}$ mol/L, 298 K).
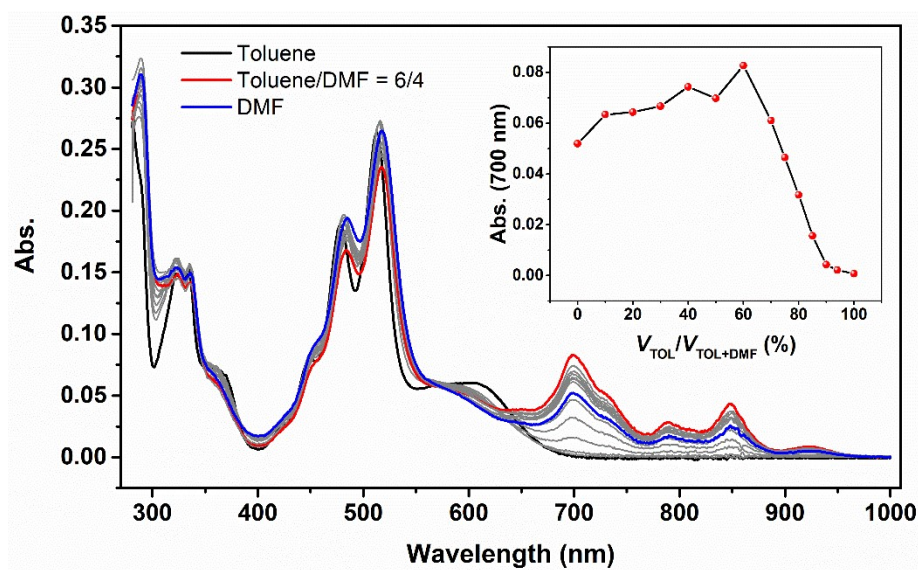
Figure S5. UV-Vis-NIR absorption spectra of PBI-4Cz in the binary mixture of DMF and toluene ($C \sim 5.0 \times 10^{-6}$ mol/L, 298 K). *Inset*: Plot of absorbance at 700 nm versus the content of toluene.

Table S1. Summarized electrochemical properties of PBI-4Cz and Ref-PBI.[4]

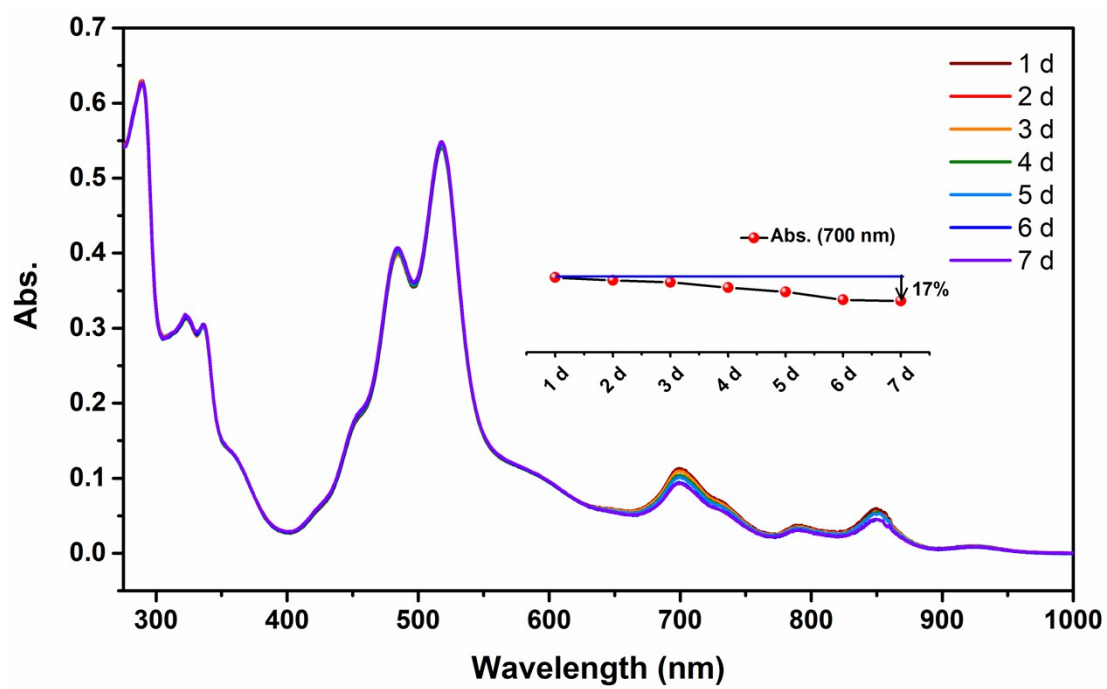| Compound	$E_{1st-red}$ /V	$E_{2nd-red}$ /V	E_{LUMO} /eV
PBI-4Cz	-0.87	-1.20	-3.93
Ref-PBI	-1.10	-1.30	-3.70

Figure S6. Time-dependent UV-Vis-NIR spectra of PBI-4Cz in DMF under ambient air (C~1.0×10^{-5} mol/L, 298 K).
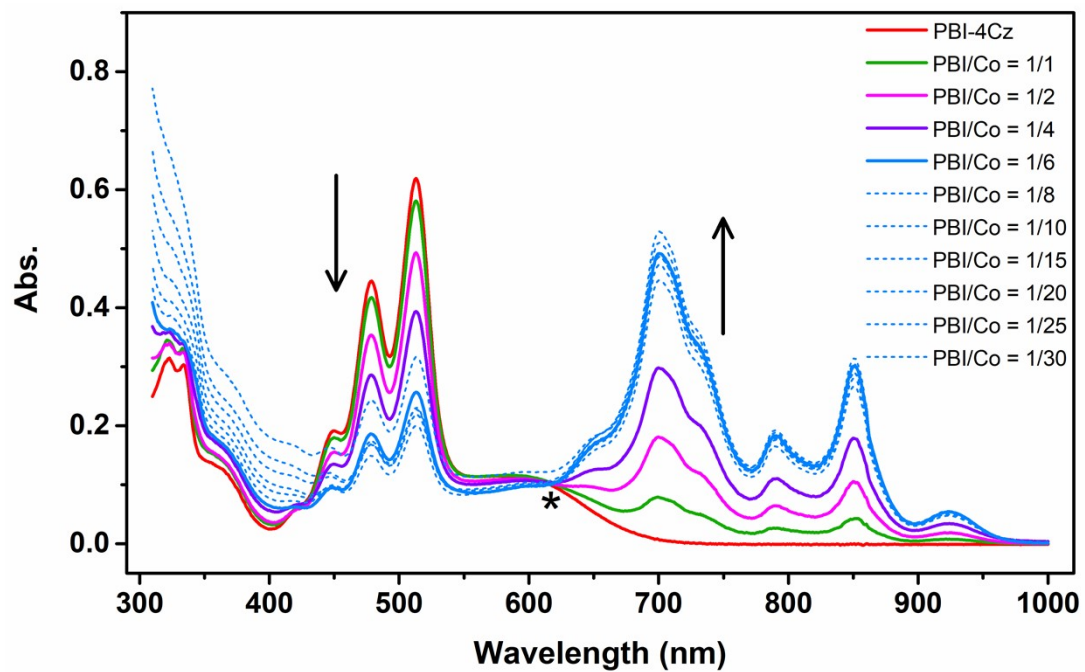
Figure S7. UV-Vis-NIR absorption spectra of PBI-4Cz in CH_2Cl_2 ($C \sim 1.0 \times 10^{-5}$ mol/L, 298 K) upon gradual addition of $CoCp_2$.

Table S2. Crystal data and structure refinement for [PBI-4Cz]·(CoCp$_2$)$_2$

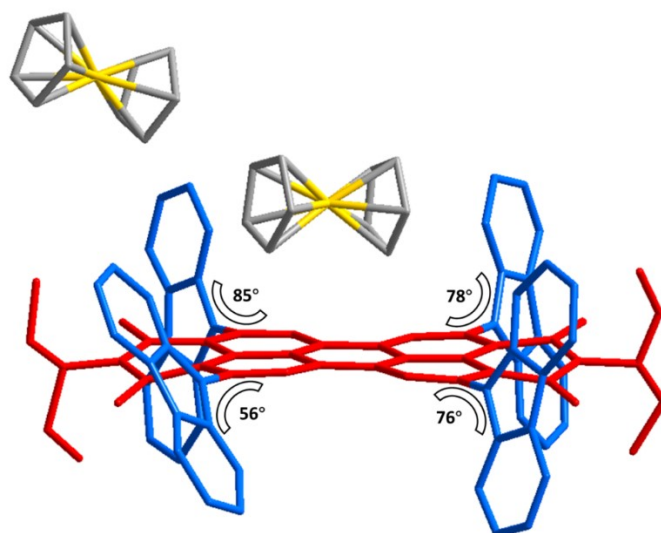|	
Identification code	[PBI-4Cz]·(CoCp$_2$)$_2$
Empirical formula	C$_{105}$H$_{87}$Co$_2$N$_7$O$_5$
Formula weight	1644.67
Temperature	235(2) K
Wavelength	1.34139 Å
Crystal system	Orthorhombic
Space group	P2$_1$2$_1$2$_1$
Unit cell dimensions	a = 18.044(10) Å α = 90 $^\circ$
	b = 32.231(19) Å β = 90 $^\circ$
	c = 16.800(9) Å γ = 90 $^\circ$
Volume	9770(10) Å^3
Z	4
Density (calculated)	1.118 mg/m^3
Absorption coefficient	2.129 mm^{-1}
F(000)	3440
Crystal size	0.100 × 0.100 × 0.100 mm^3
Theta range for data collection	2.385 to 51.587 $^\circ$
Index ranges	-20≤h≤19, -32≤k≤37, -19≤l≤19
Reflections collected	71096
Independent reflections	15928 [R(int) = 0.2030]
Completeness to theta = 51.587 $^\circ$	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7501 and 0.5565
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15928/828/1042
Goodness-of-fit on F^2	0.901
Final R indices [I>2sigma(I)]	R$_1$ = 0.0911, wR$_2$ = 0.2116
R indices (all data)	R$_1$ = 0.2599, wR$_2$ = 0.2967
Absolute structure parameter	0.446(16)
Extinction coefficient	n/a
Largest diff. peak and hole	0.220 and -0.254 e.Å^{-3}

Figure S8. Dihedral angles between the plane of PBI and four carbazole moieties.
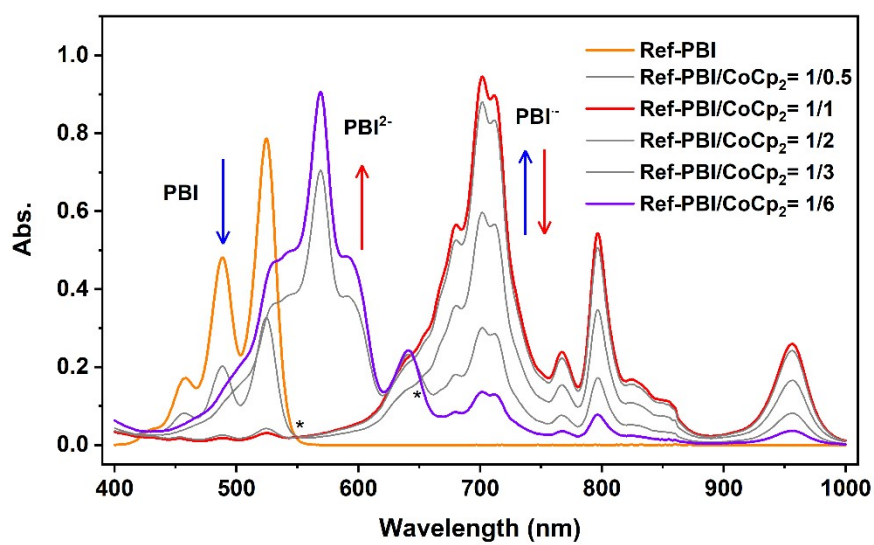
Figure S9. UV-Vis-NIR absorption spectra of Ref-PBI in DMF (C~1.0×10^{-5} mol/L, 298 K) upon gradual addition of CoCp$_2$. *Note*: The isobestic points were marked with asterisk.
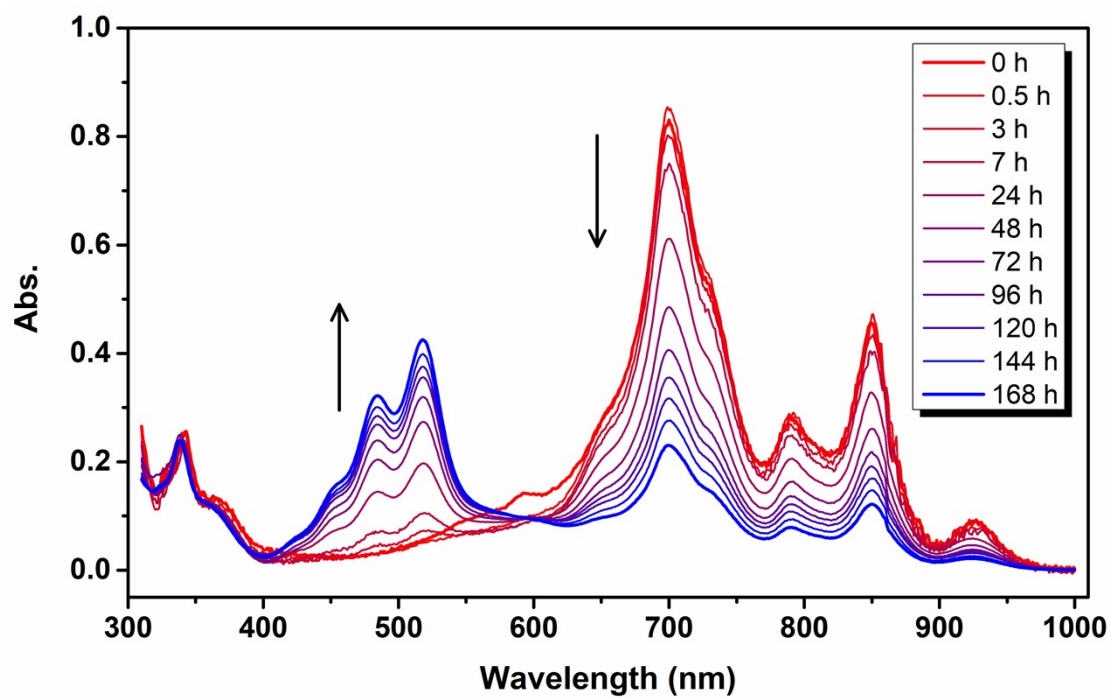
Figure S10. Time-dependent UV-Vis-NIR spectra of the fresh PBI$^{\cdot-}$-4Cz in DMF under ambient air (C~1.0 × 10^{-5} mol/L, 298 K). Note: The fresh PBI$^{\cdot-}$-4Cz was obtained via chemically reduced method by CoCp$_2$.
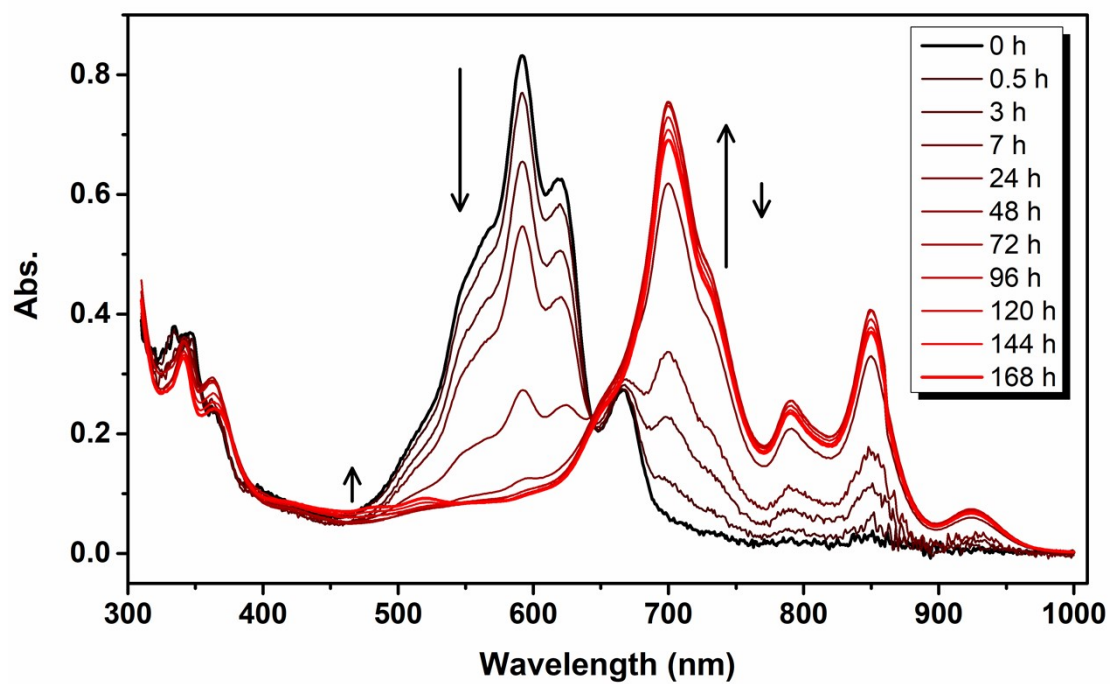
Figure S11. Time-dependent UV-Vis-NIR spectra of PBI^{2-}-4Cz in DMF under ambient air (C~1.0 × 10^{-5} mol/L, 298 K).
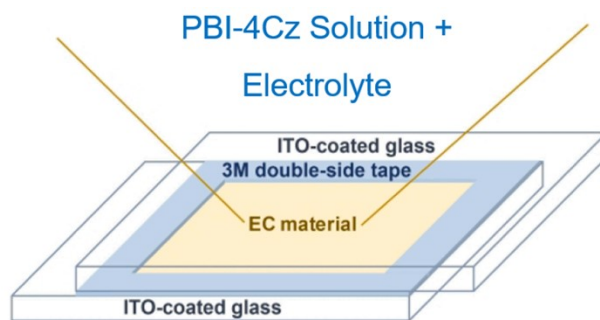
Figure S12. Schematic illustration of the PBI-4Cz solution-based electrochromic device.[5]

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