ELECTRONIC SUPPLEMENATRY INFORMATION

Tunable electronic interactions between anions and perylenediimide

Flynt S. Goodson,[a] Dillip K. Panda,[a] Shuvasree Ray,[a] Atanu Mitra,[a] Samit Guha[a] and Sourav Saha*

Department of Chemistry and Biochemistry and Integrative NanoScience Institute, Florida State University, 95 Chieftan Way, Tallahassee, Florida 32306, United States

Email: saha@chem.fsu.edu

EXPERIMENTAL SECTION

MATERIALS

Chemicals and solvents were purchased from Sigma-Aldrich, Acros Organic, Cambridge Isotope Laboratory, and EMD Chemicals and used as obtained. **PDI-1** was synthesized and characterized according to a literature procedure.[S1] Tetra-*n*-butylammonium (TBA) salts of F^-, Cl^-, Br^-, I^-, OH^-, and PF_6^- were purchased from Sigma-Aldrich and were protected from moisture. Freshly prepared solutions of **PDI-1** and anions in dry, HPLC grade solvents — purchased from Sigma-Aldrich and EMD Chemicals — were used for all spectroscopic and electrochemical measurements.

METHODS

UV/Vis Spectroscopy

UV/Vis spectra of **PDI-1** was recorded on a PerkinElmer Lambda-25 UV/Vis spectrophotometer in different solvents and in the presence and absence of anions.

Electrochemistry

Cyclic voltammetry (CV) of **PDI-1** was conducted on a Princeton Applied Research (PAR) VersaStat-3-200 potentiostat/galvanostat instrument using a standard electrochemical cell, consisting of a glassy carbon working electrode, Pt-wire counter electrode, and Ag/AgCl (3 N aq. NaCl) reference electrode. CV was recorded for 1 mM PDI solutions in the presence of 0.1M $TBAPF_6$ in THF, and Acetone at room temperature with 100 mV/s scan rate.

Spectroelectrochemistry

Spectroelectrochemistry was conducted in an Optically Transparent Thin Layer Electrochemical Cell (OTTLE) fitted with a Pt-gauge working electrode, Pt-wire counter electrode, and Ag/AgCl (3 N aq. NaCl) reference electrode using degassed (N_2-purged) 0.1 mM solutions of **PDI-1** in 0.1 M $TBAPF_6$ in THF and DMF at room temperature. UV/Vis spectra were recorded at 2 min. intervals on a PerkinElmer Lambda-25 UV/Vis spectrophotometer while the applied potential (V_{ap}) was controlled by the PAR potentiostat, using Virtual Potentiostat software. **PDI-1**$^{\bullet-}$ radical anion started to form at V_{ap} = –550 mV (vs. Ag/AgCl) and saturated at –1100 mV.

NMR Experiments

^1H and ^{19}F NMR titrations were conducted at 298 K in appropriate deuterated solvents (THF-d_8 and $(CD_3)_2CO$) using Bruker Avance 400 MHz and Bruker Avance 600 MHz spectrometers. For titrations, the concentration of **PDI-1** solutions were maintained at 1 mM and the stock solutions of TBAX salts were made 10 times concentrated.

EPR Spectroscopy

EPR spectra of neutral **PDI-1** (1 mM) and F^--generated **PDI-1**$^{\bullet-}$ radical anion were recorded in THF and DMF using a Bruker Elexsys-500 spectrometer, at the X-band, microwave frequency 9.3902 GHz; microwave power 1 mw; and modulation amplitude 1 Gauss (G) at 298 K. The microwave frequency was measured with a built-in digital counter and the magnetic field was calibrated using 2, 2-diphenyl-1-picrylhydrazyl (DPPH; g = 2.0037). Modulation amplitude and microwave power were optimized for high signal-to-noise ratio and narrow peaks.[S2]

REFERENCE.

S1. (a) S. Rajaram, P. B. Armstrong, B. J. Kim and J. M. J. Fréchet, *Chem. Mater.*, 2009, **21**, 1775; (b) D. K. Panda, F. S. Goodson, S. Ray, R. Lowell and S. Saha*, Chem. Commun*. 2012, **48**, 8775.

S2. (a) G. Andric, J. F. Boas, A. M. Bond, G. D. Fallon, K. P. Ghiggino, C. F. Hogan, J. A. Hutchison, M. A. -P. Lee, S. J. Langford, J. R. Pilbrow, G. J. Troup and C. P. Woodward, *Aust. J. Chem*. 2004, **57**, 1011; (b) Y. Che, A. Datar, X. Yang, T. Naddo, J. Zhao and L. Zang, *J. Am. Chem. Soc.,* 2007, **129**, 6354; (c) S. Fukuzumi, K. Ohkubo, J. Ortiz, A. M. Gutiérrez, F. Fernández-Lázaro and Á. Sastre-Santos, *J. Phys. Chem. A,* 2008, **112**, 10744; (d) M. Supur, Y. Yamada, M. E. El-Khouly, T. Honda and S. Fukuzumi, *J. Phys. Chem. B,* 2011, **115**, 15040; (e) S. Guha, F. S. Goodson, L. J. Corson and S. Saha, *J. Am. Chem. Soc.,* 2012, **134**, 13679.

Additional Figures

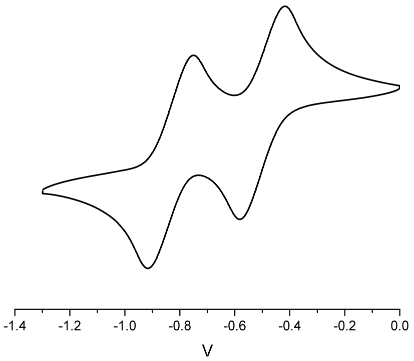

Fig S1. Cyclic voltammogram of **PDI-1** (1 mM **PDI-1** in 0.1 M $TBAPF_6$ / THF, vs. Ag/AgCl, scan rate = 100 mV/s) shows two fully reversible reduction waves.

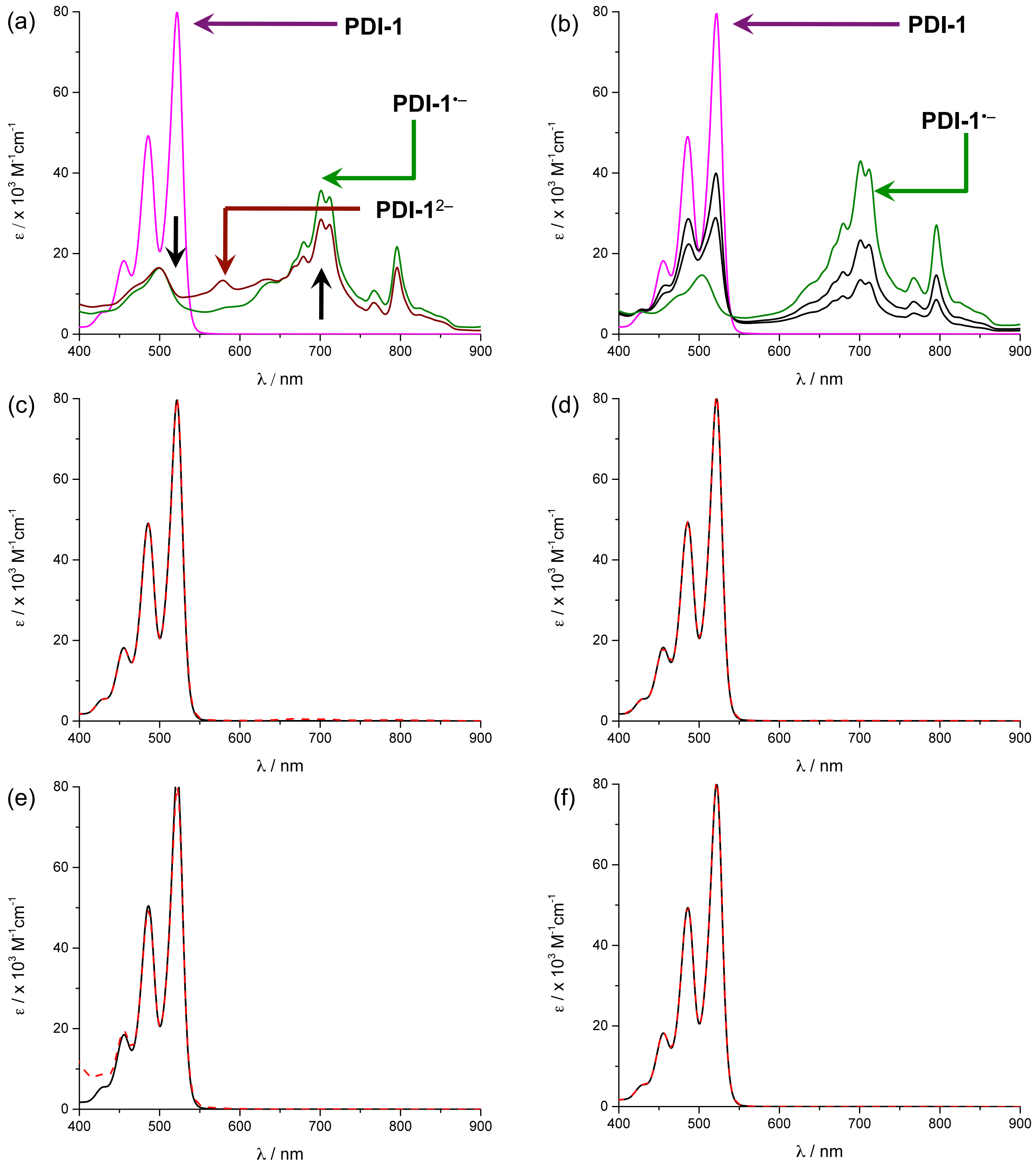

Fig S2: UV/Vis titrations of **PDI-1** in THF with: (a) TBAOH: pink trace: neutral **PDI-1** (no OH^-), green trace: **PDI-1**$^{\bullet-}$ radical anion (8 equiv. OH^-), red trace: (100 equiv. OH^-); (b) TBAF: pink trace: neutral **PDI-1** (no F^-), green trace: **PDI-1**$^{\bullet-}$ radical anion (1–100 equiv. F^-); (c–f) TBACl, TBABr, TBAI, and $TBAPF_6$: black traces: neutral **PDI-1** (no anion), overlapping dashed red lines: **PDI-1** in the presence of 100 equiv. of (c) Cl^-, (d) Br^-, (e) I^-, and (f) PF_6^- indicating no ET and CT interactions.

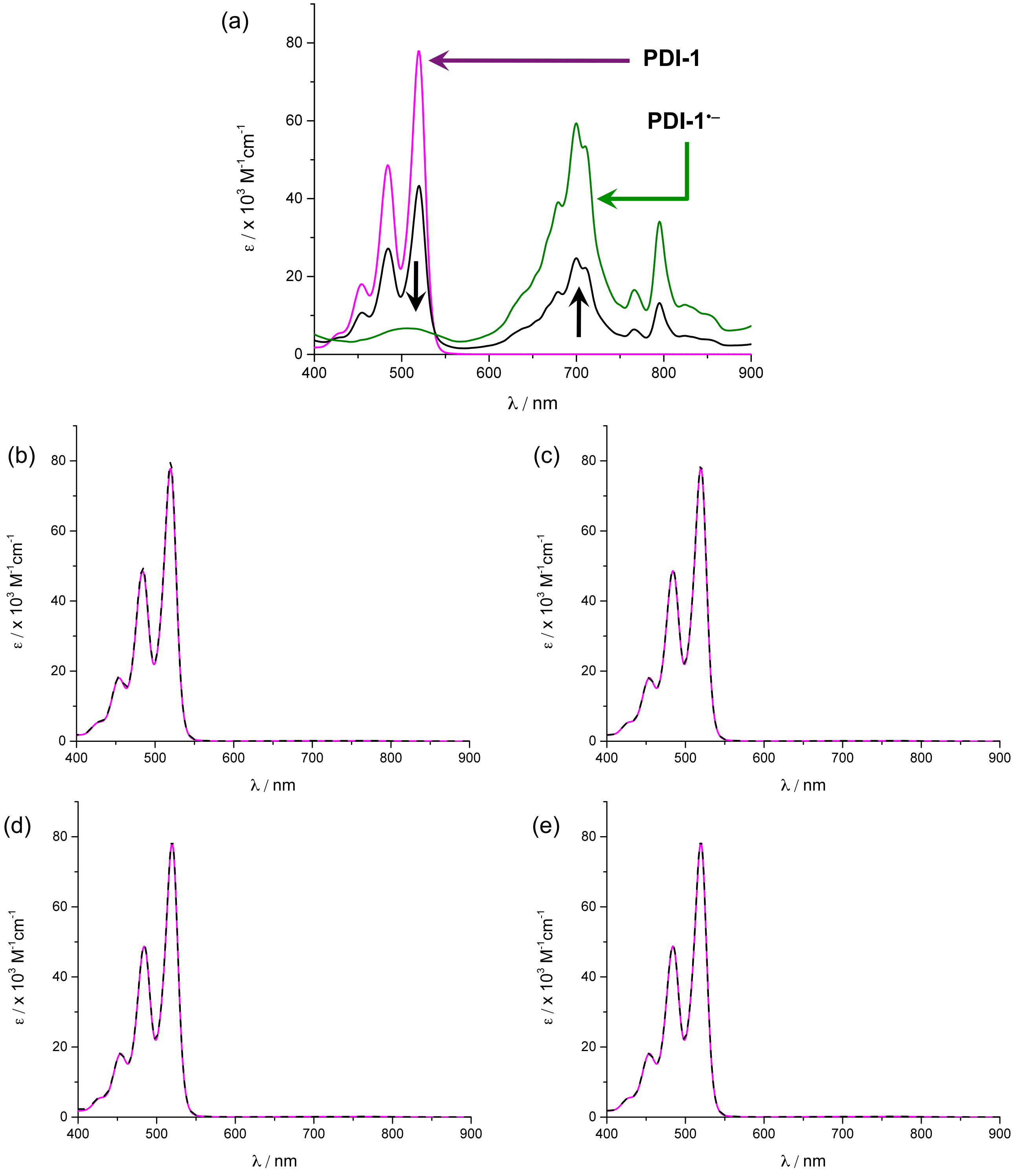

Fig S3: UV/Vis titrations of **PDI-1** in Me$_2$CO with: (a) TBAF: pink trace: neutral **PDI-1** (no F$^-$), green trace: **PDI-1**$^{\bullet -}$ radical anion (1–100 equiv. F$^-$); (b–e) TBACl, TBABr, TBAI, and TBAPF$_6$: pink traces: neutral **PDI-1** (no anion), overlapping dashed black lines: **PDI-1** in the presence of 100 equiv. of (c) Cl$^-$, (d) Br$^-$, (e) I$^-$, and (f) PF$_6^-$ indicating no ET and CT interactions. Ttitration with TBAOH could not be conducted in Me$_2$CO.

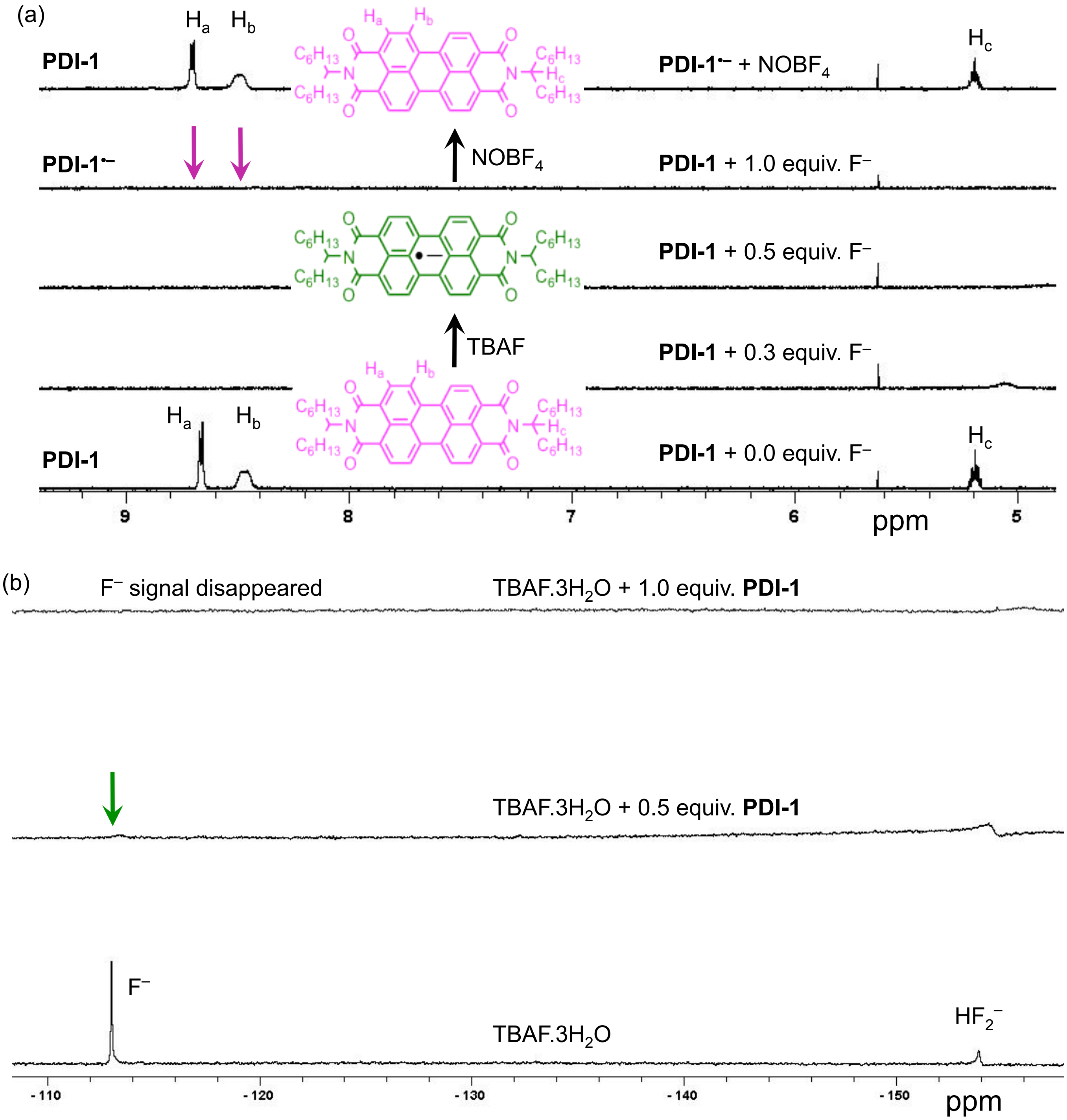

Fig S4: (a) ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 25 °C) titration of **PDI-1** with TBAF. **PDI-1** signals disappeared in the presence of TBAF but no new peak emerged, indicating the formation of paramagnetic **PDI-1**$^{\bullet-}$ radical anion, which was oxidized back to neutral **PDI-1** by $NOBF_4$, as characteristic signals reappeared. (b) ^{19}F NMR (400 MHz, $(CD_3)_2CO$, 25 °C) titration of TBAF. $3H_2O$ with **PDI-1**. The F^- signal disappeared in the presence of 1 equiv. of **PDI-1**, indicating the oxidation of F^- to a sacrificial $F^\bullet$ radical. The lack of any new F-signal ruled out covalent C–F bond formation.

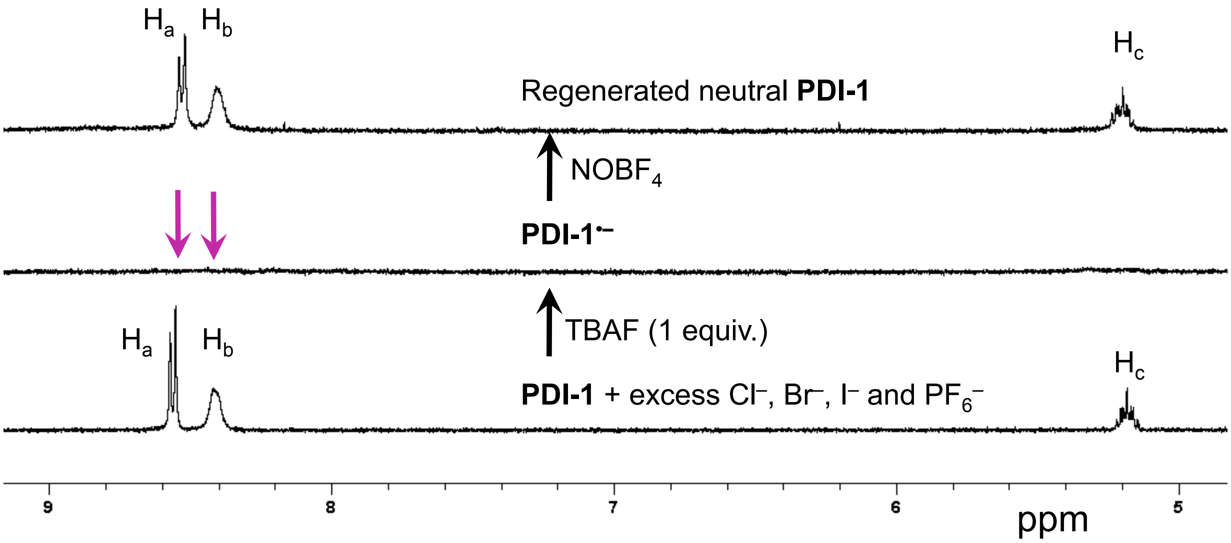

Fig S5: ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 25 °C) of **PDI-1** in the presence of excess amounts of TBA$^+$ salts of Cl$^-$, Br$^-$, I$^-$ and PF_6^- (bottom spectrum: neutral **PDI-1**), upon addition of 1 equiv. of TBAF into the solution (middle spectrum: **PDI-1**$^{\bullet-}$ formation), and upon addition of $NOBF_4$ to the F$^-$-generated **PDI-1**$^{\bullet-}$ radical anion (top spectrum: **PDI-1** regeneration).

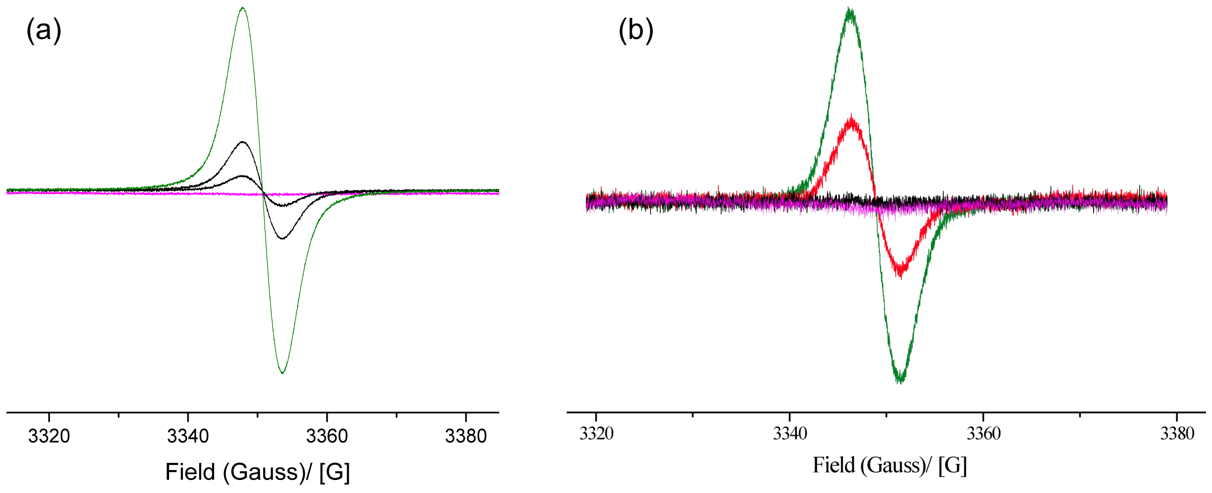

Fig S6: (a) EPR spectra (THF, 25 °C) of neutral **PDI-1** (pink trace, no signal) and **PDI-1**$^{\bullet-}$ radical anion produced by increasing amounts of TBAF (1, 1.5, 2 equiv.). (b) EPR spectra (DMF, 25 °C) of neutral **PDI-1** (pink trace, no signal), **PDI-1**$^{\bullet-}$ radical anion produced by 10 equiv. of TBAOH (green trace), and gradual disappearance of **PDI-1**$^{\bullet-}$ radical anion with excess TBAOH (red trace: 100 equiv. TBAOH and black trace (no signal): 500 equiv. TBAOH) upon formation of diamagnetic **PDI-1**$^{2-}$ dianion.