

# Initiation of Radical Photopolymerization with Perylenebisimide Derivatives Having Twisted Molecular Structures as Heavy-Atom-free Visible Light-Harvesting Efficient Photoinitiators

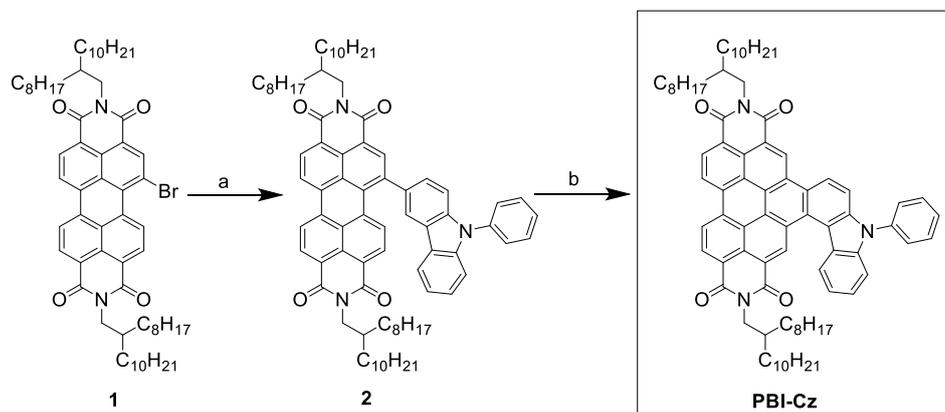
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## Molecular Synthesis and Structure Characterization Data<sup>a</sup>



<sup>a</sup> Key: (a) 9-phenyl-9H-carbazol-3-ylboronic acid, K<sub>2</sub>CO<sub>3</sub>, PhCH<sub>3</sub>/C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O (4:2:1, v/v), Pd(PPh<sub>3</sub>)<sub>4</sub>, N<sub>2</sub>, reflux at 80 °C, 8 h, yield: 95%; (b) *hν*, I<sub>2</sub>, PhCH<sub>3</sub>, 25 °C, 36 h, yield: 57%. The molecular structures of the photoinitiators (PIs) **PBI**, **PBI-Cz** and **DiPBI**. The molecular structures of the co-initiators (NB and DPI) and the monomer trimethylolpropane triacrylate (TMPTA) are also presented.

*Synthesis of Compound 2.* The compound was prepared with a literature method [1]. A mixture of compound 1 (100 mg, 97.06 μmol), 9-phenyl-9H-carbazol-3-ylboronic acid (55.7 mg, 0.2 mmol), K<sub>2</sub>CO<sub>3</sub> (60.36 mg, 0.44 mmol) in solvent of PhCH<sub>3</sub>/EtOH/H<sub>2</sub>O (4/2/1, v/v, 25 mL) was deoxygenated by using N<sub>2</sub> bubbling for 25 minutes. Then Pd(PPh<sub>3</sub>)<sub>4</sub> (20 mg, 5 mmol %) was added and the reaction mixture was heated at 80 °C under N<sub>2</sub> for 8 h. The cooled mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed with water (2 × 100 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The crude solid was purified by column chromatography (silica gel, dichloromethane (DCM)/petroleum ether (PE) = 1:2, v/v) to give a red solid (78 mg, yield: 67.4%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.63 (d, 2H, *J* = 8.0 Hz), 8.54 (s, d, 2H, *J* = 8.0 Hz), 8.47 (s, d, 2H, *J* = 8.0 Hz), 8.42 (s, d, 2H, *J* = 8.0 Hz), 8.33 (s, 1H), 8.18 (d, 2H, *J* = 8.0 Hz), 7.98 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.68–7.64 (t, 4H, *J* = 8.0 Hz), 7.52 (d, 2H, *J* = 8.0 Hz), 7.48 (d, 2H, *J* = 4.0 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.35–7.31 (m, 2H), 4.14 (d, *J* = 8.0 Hz, 2H), 4.05 (d, *J* = 8.0 Hz, 2H), 2.01–1.95 (m, 2H), 1.25–1.21 (m,



64H), 0.83 (s, 12H). HRMS (MALDI,  $m/z$ ) calcd for  $[\text{C}_{82}\text{H}_{101}\text{N}_3\text{O}_4]^+$ : calcd  $m/z = 1191.7787$ , found  $m/z = 1191.7766$ .

**Synthesis of PBI-Cz.** The compound was prepared by using a reported method [1]. Compound **2** (70 mg, 58.69  $\mu\text{mol}$ ) and  $\text{I}_2$  (11.8 mg, 46.36  $\mu\text{mol}$ ) were dissolved in toluene (30 mL). The solution was photo-irradiated by white light (xenon lamp) for 36 h at room temperature. After the completion of the reaction, the reaction mixture was concentrated under reduced pressure to obtain the crude product, which was further purified by column chromatography (silica gel, DCM/PE = 1:1, v/v) to obtain as a dark red solid (20 mg, yield: 28%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 9.51$  (s, 2H), 9.13 (s, 1H), 9.06 (d, 1H,  $J = 8.0$  Hz), 8.62 (d,  $J = 8.0$  Hz, 1H), 8.52 (d, 1H,  $J = 8.0$  Hz), 8.47 (t,  $J = 8.0$  Hz, 2H), 8.18 (d, 3H,  $J = 8.0$  Hz), 7.78 (d, 2H,  $J = 8.0$  Hz), 7.51 (t,  $J = 6.0$  Hz, 2H), 7.39 (d, 2H,  $J = 8.0$  Hz), 4.23 (t,  $J = 6.0$  Hz, 4H), 2.05 (s, 2H), 1.26–1.18 (m, 64H), 0.82–0.77 (m, 12H). HRMS (MALDI,  $m/z$ ) calcd for  $[\text{C}_{82}\text{H}_{99}\text{N}_3\text{O}_4]^-$ : calcd  $m/z = 1189.7636$ , found  $m/z = 1189.7592$ .

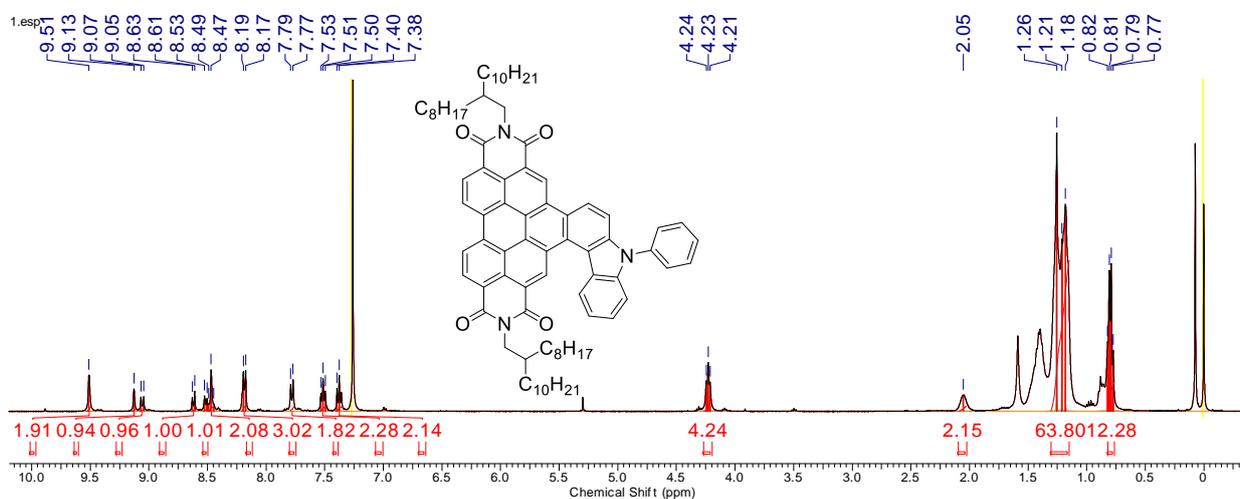


Figure S1.  $^1\text{H}$  NMR spectrum of compound **PBI-Cz** (400 MHz,  $\text{CDCl}_3$ ), 25  $^\circ\text{C}$ .

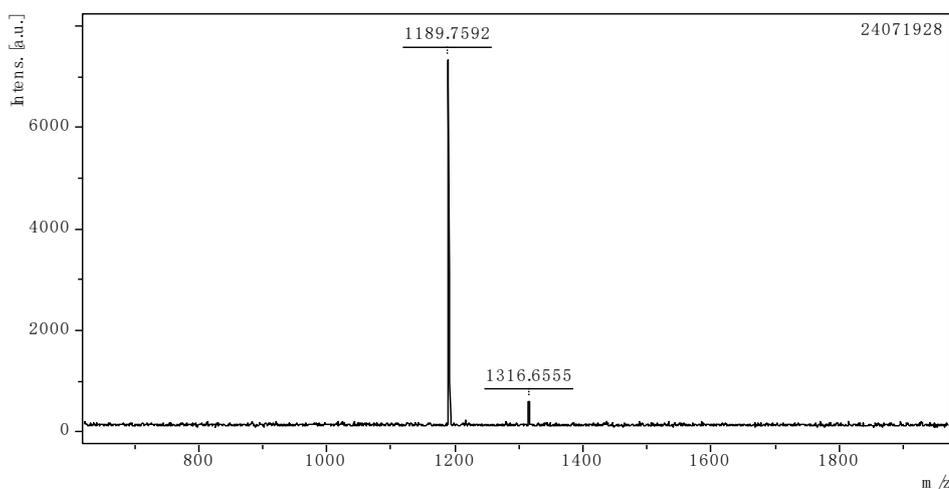
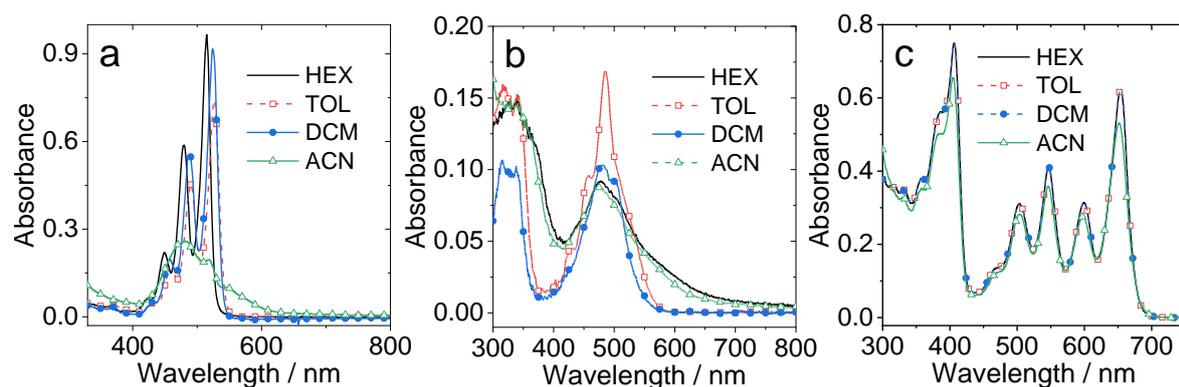
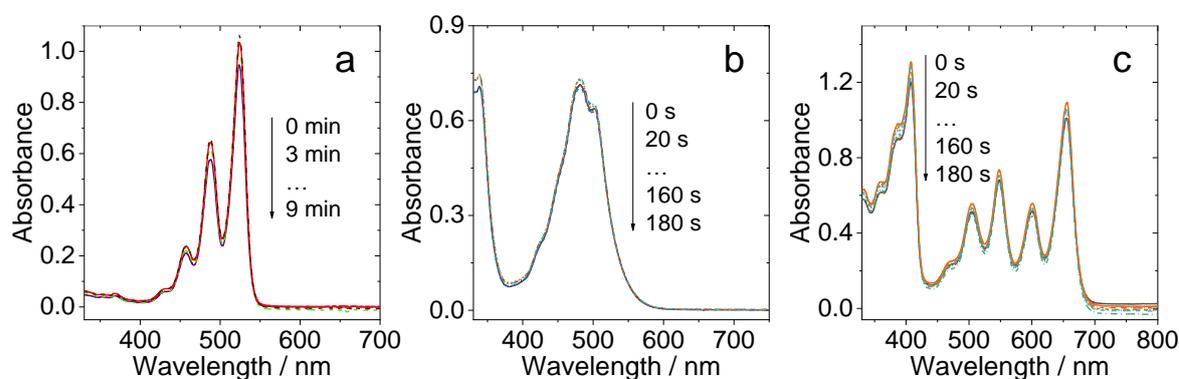


Figure S2. MALDI HR MS of compound **PBI-Cz**. 25  $^\circ\text{C}$ .

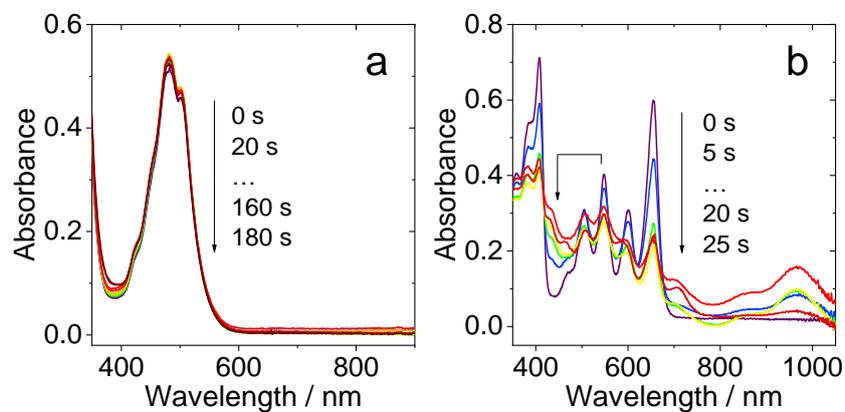
## Steady State UV–Vis Absorption and Photobleaching



**Figure S3.** UV-vis absorption spectra of (a) **PBI**, (b) **PBI-Cz** and (c) **DiPBI** in different solvents,  $c = 1.0 \times 10^{-5}$  M, 25 °C.

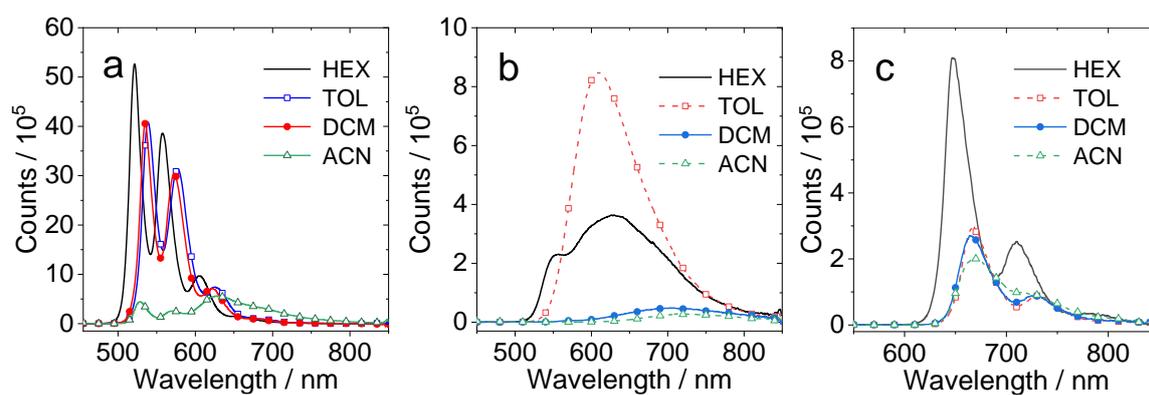


**Figure S4.** UV-vis absorption spectra of (a) **PBI** ( $1.0 \times 10^{-5}$  M), (b) **PBI-Cz** ( $5.0 \times 10^{-5}$  M) and (c) **DiPBI** ( $1.5 \times 10^{-5}$  M) upon 532 nm LED exposure in the presence of DPI (6 eq.) in deaerated DCM, the power density is 5 mW/cm<sup>2</sup>, 25 °C.

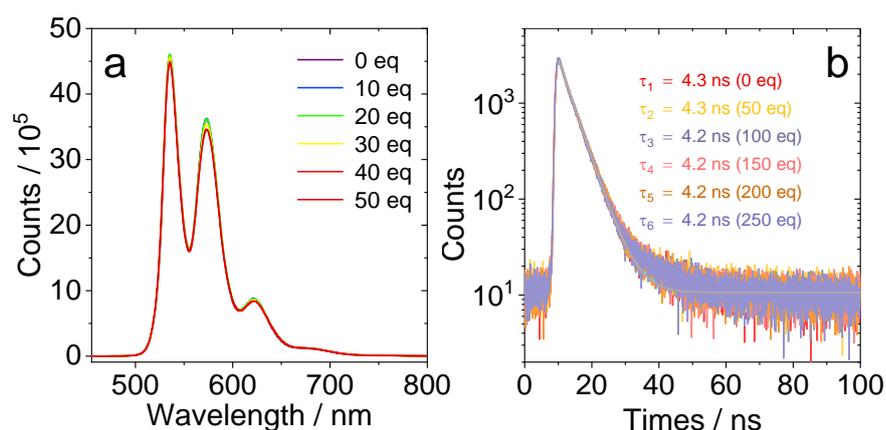


**Figure S5.** UV-vis absorption spectra of (a) **PBI-Cz** ( $5.0 \times 10^{-5}$  M) and (b) **DiPBI** ( $1. \times 10^{-5}$  M) upon 532 nm LED exposure in the presence of NB (6 eq.) and DPI (6 eq.) in deaerated DCM, the power density is 5 mW/cm<sup>2</sup>, 25 °C.

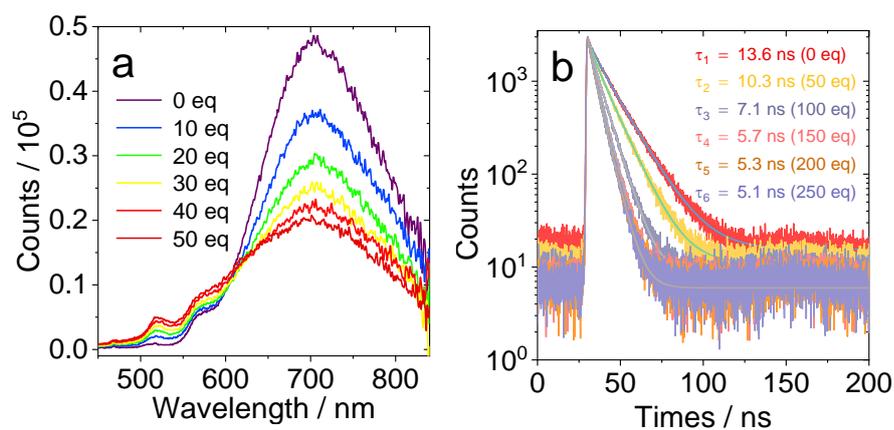
### Fluorescence and Fluorescence Lifetime quenching



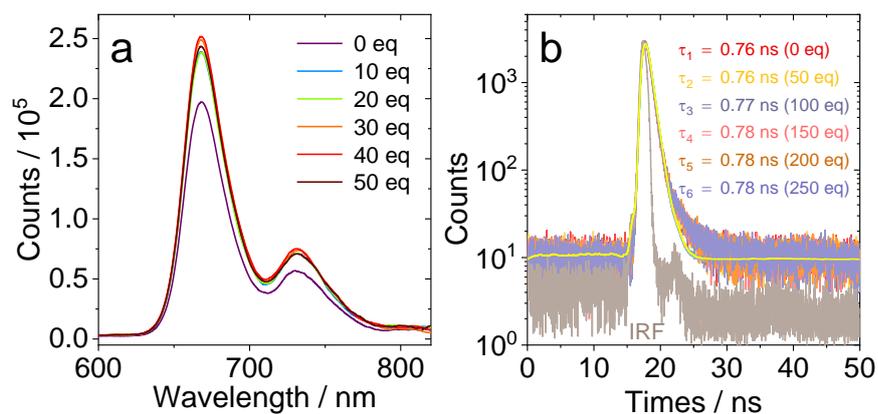
**Figure S6.** Fluorescence spectra of (a) **PBI** ( $\lambda_{\text{ex}} = 445$  nm), (b) **PBI-Cz** ( $\lambda_{\text{ex}} = 410$  nm) and (c) **DiPBI** ( $\lambda_{\text{ex}} = 410$  nm) in different solvents,  $A = 0.10$ . Optically matched solutions were used in each panel (each of the solutions gives the same absorbance at the excitation wavelength), 25 °C.



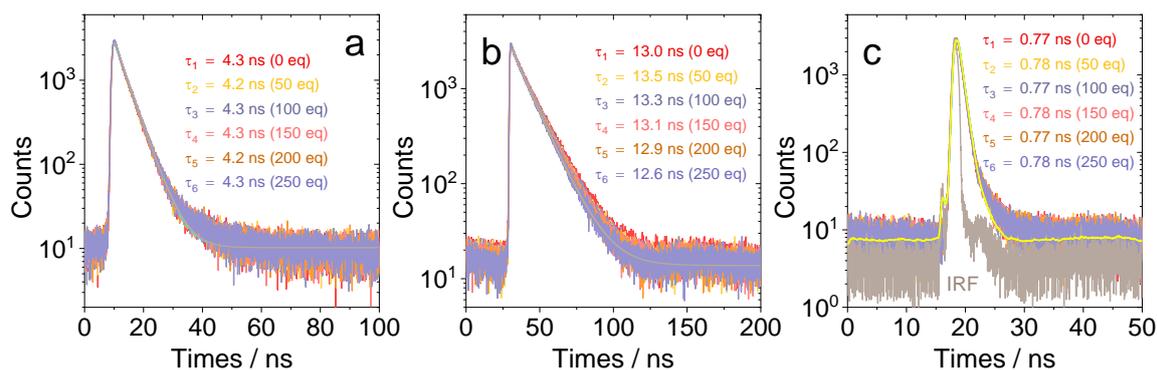
**Figure S7.** (a) Fluorescence quenching spectra and (b) fluorescence decay traces of **PBI** under Air atmospheres in DCM upon the increasing addition of NB.  $\lambda_{\text{ex}} = 445 \text{ nm}$ ,  $A = 0.10$ ,  $c = 1.0 \times 10^{-5} \text{ M}$ ,  $25 \text{ }^\circ\text{C}$ .



**Figure S8.** (a) Fluorescence quenching spectra ( $\lambda_{\text{ex}} = 410 \text{ nm}$ ) and (b) fluorescence decay traces of **PBI-Cz** ( $\lambda_{\text{ex}} = 405 \text{ nm}$ ) under Air atmospheres in DCM upon the increasing addition of NB,  $A = 0.10$ ,  $c = 1.0 \times 10^{-5} \text{ M}$ ,  $25 \text{ }^\circ\text{C}$ .



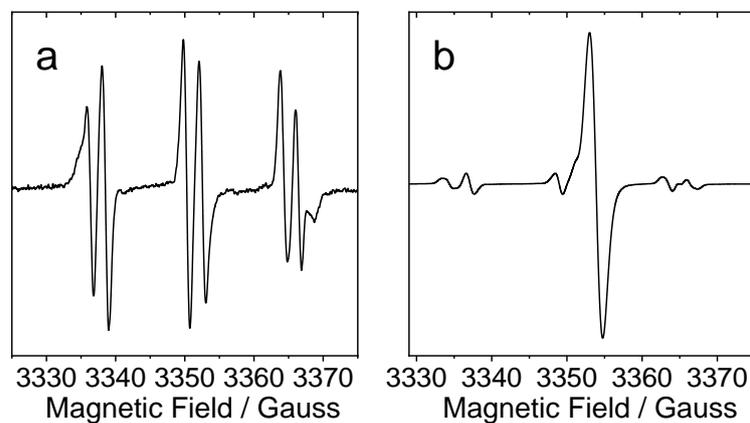
**Figure S9.** (a) Fluorescence quenching spectra ( $\lambda_{\text{ex}} = 410$  nm) and (b) fluorescence decay traces of **DiPBI** ( $\lambda_{\text{ex}} = 405$  nm) under Air atmospheres in TOL upon the increasing addition of NB.,  $A = 0.10$ ,  $c = 1.0 \times 10^{-5}$  M, 25 °C.



**Figure S10.** Fluorescence decay traces of (a) **PBI** ( $\lambda_{\text{ex}} = 445$  nm), (b) **PBI-Cz** ( $\lambda_{\text{ex}} = 405$  nm) and (c) **DiPBI** ( $\lambda_{\text{ex}} = 405$  nm) under Air atmospheres in TOL upon the increasing addition of DPI.  $\lambda_{\text{ex}} = 410$  nm,  $c = 1.0 \times 10^{-5}$  M, 25 °C.

## Electron Paramagnetic Resonance (EPR) Spectra

EPR experiment was performed using a Bruker ELEXSYS-II E500 CW-EPR. PSs ( $2.0 \times 10^{-4}$  mol/L), NB (0.1 mol/L) and *N*-tert-Butyl- $\alpha$ -phenylnitron (PBN) ( $4.0 \times 10^{-2}$  mol/L) as radicals trap were dissolved in DCM as free radical traps. Oxygen was then removed from the solution by bubbling with  $N_2$  for 10 min. 532 nm LED was used as an irradiation source to trigger radical production at room temperature.



**Figure S11.** EPR spectra of (a) **PBI-Cz**/NB/PBN and (b) **DiPBI**/NB/PBN mixed solution in deaerated DCM.  $c[\text{Sample}] = 1.0 \times 10^{-4}$  M,  $c[\text{NB}] = 1.0 \times 10^{-2}$  M,  $c[\text{PBN}] = 2.0 \times 10^{-2}$  M, 25 °C.

## References

1. Mahmood, Z.; Sukhanov, A. A.; Rehmat, N.; Hu, M.; Elmali, A.; Xiao, Y.; Zhao, J.; Karatay, A.; Dick, B.; and Voronkova, Violeta K. Intersystem crossing and triplet state property of anthryl- and carbazole-[1,12]fused perylenebisimide derivatives with twisted  $\pi$ -conjugation Framework. *J. Phys. Chem. B*, **2021**, *125*, 9317–9332. <https://doi.org/10.1021/acs.jpcc.1c05032>.