

## Supporting Information

# Re-examining the Photomediated Dissociation and Recombination Kinetics of Hexaarylbiimidazoles

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### *p*-HOH-HABI Synthesis

#### *Synthesis of 2-Chloro-4-((6-hydroxyhexyl)oxy)benzaldehyde (2).*

2-Chloro-4-hydroxybenzaldehyde (10.0 g, 63.9 mmol) and potassium carbonate (26.5 g, 192 mmol) were added to 150 mL of DMF and the mixture stirred. 6-Chlorohexanol (11.1 mL, 83.0 mmol) was then added and the mixture heated at 120°C for 16 hours under nitrogen. After cooling to room temperature, the mixture was filtered to remove potassium carbonate, DMF was evaporated under reduced pressure, and the residue was carefully distilled, removing the excess 6-chlorohexanol, yielding 15.0 g of **2** (91.6% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ: 1.31-1.45 (m, 6H), 1.69-1.75 (m, 2H), 3.35-3.41 (q, 2H), 4.08-4.12 (t, 2H), 4.34-4.37 (t, 1H), 7.05-7.08 (q, 1H), 7.16-7.17 (d, 1H), 7.80-7.82 (d, 1H), 10.18 (s, 1H).

#### *Synthesis of 6-(3-Chloro-4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexyl acetate (3).*

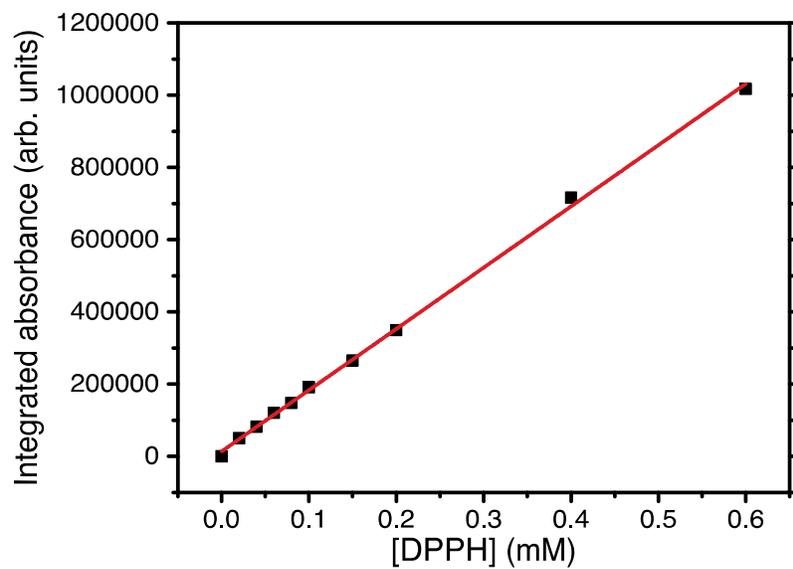
A mixture of **2** (10.0 g, 39.0 mmol), benzil (8.19 g, 39.0 mmol), ammonium acetate (25.4 g, 330 mmol), and acetic acid (150 mL) was refluxed for 16 hours under nitrogen. After cooling to room temperature, the solvent was partially removed under reduced pressure and poured into 10-fold water. The generated brown-yellow precipitate was filtered, washed with water, and dried. The precipitate was recrystallized in ethanol/water, yielding 11.2 g of **3** (58.7% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ: 1.35-1.47 (m, 4H), 1.57-1.63 (m, 2H), 1.71-1.78 (m, 2H), 2.00 (s, 3H), 4.00-4.02 (t, 2H), 4.04-4.08 (t, 2H), 7.03-7.05 (q, 1H), 7.15-7.16 (d, 1H), 7.22-7.23 (d, 1H), 7.24-7.32 (t, 2H), 7.35-7.36 (d, 1H), 7.40-7.43 (t, 2H), 7.47-7.49 (d, 2H), 7.52-7.54 (d, 2H), 7.68-7.70 (d, 1H), 12.49 (s, 1H).

#### *6-(3-Chloro-4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexan-1-ol (4).*

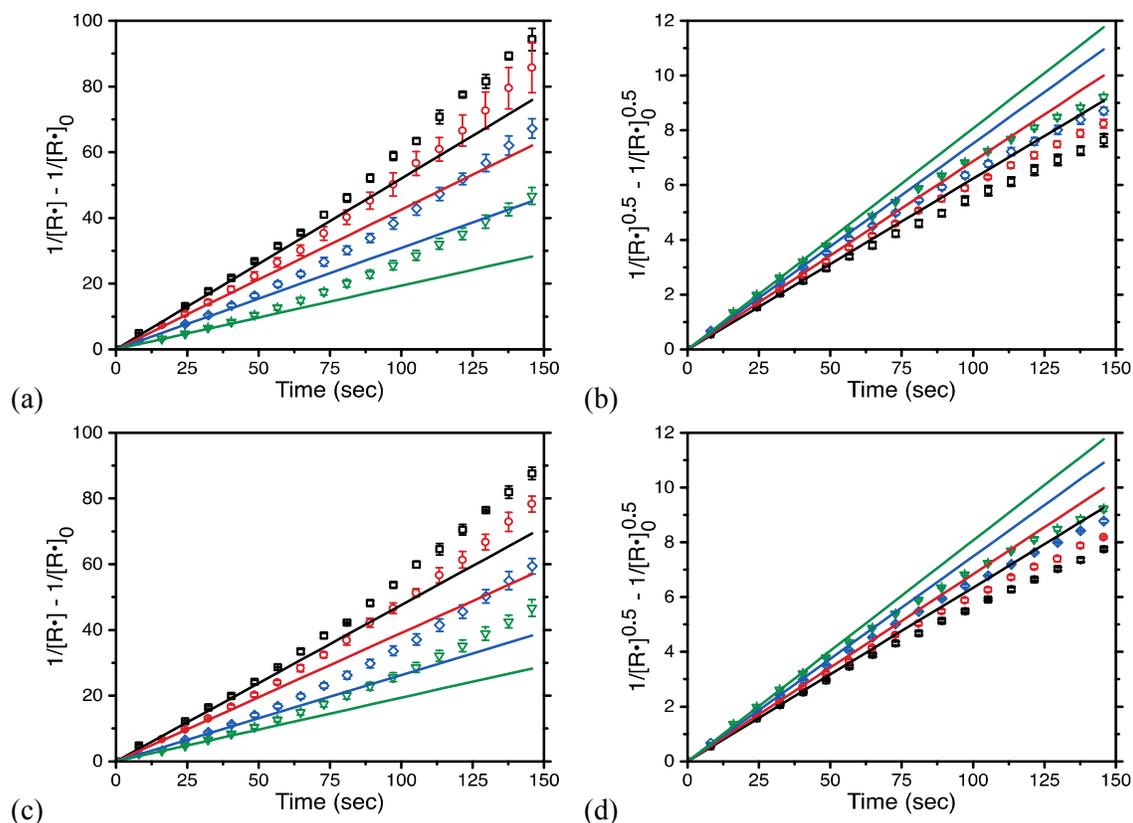
A solution of **3** (3.00 g, 6.13 mmol) in tetrahydrofuran (THF) (10 mL) was mixed with 3 M NaOH aqueous solution (100 mL) and refluxed at 75°C for 12 hours. After cooling to room temperature, solvent was partially removed under reduced pressure and extracted with dichloromethane. The organic layer was collected, washed with brine, and dried over anhydrous magnesium sulfate. The organic solvents were removed under reduced pressure to afford a yellow powder, yielding 2.50 g of **4** (91.2% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ: 1.35-1.47 (m, 4H), 1.57-1.63 (m, 2H), 1.71-1.78 (m, 2H), 4.00-4.02 (t, 2H), 4.04-4.08 (t, 2H), 7.03-7.05 (q, 1H), 7.15-7.16 (d, 1H), 7.22-7.23 (d, 1H), 7.24-7.32 (t, 2H), 7.35-7.36 (d, 1H), 7.40-7.43 (t, 2H), 7.47-7.49 (d, 2H), 7.52-7.54 (d, 2H), 7.68-7.70 (d, 1H), 12.49 (s, 1H).

*2,2'-bis(2-chloro-4-hexan-1-ol-phenoxy)-4,4',5,5'-tetraphenyl-1,2'-biimidazole (p-HOH-HABI).*

To a vigorously stirred solution of potassium ferricyanide (3.29 g, 10.0 mmol) and potassium hydroxide (12.0 g, 214 mmol) in water (100 mL), a solution of **4** (1.00 g, 2.24 mmol) in dichloromethane (50 mL) was added dropwise under nitrogen. The mixture was refluxed at 45°C for 16 hours. After cooling to room temperature, the organic layer was collected, washed with water, dried over anhydrous magnesium sulfate, filtered, and the solvent removed under reduced pressure. The residue was recrystallized in diethyl ether/hexane, yielding 0.810 g of *p*-HOH-HABI (81.1% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ: 1.30-1.50 (m, 12H), 1.59-1.70 (m, 4H), 3.36-3.45 (m, 4H), 3.73-3.87 (m, 4H), 4.33-4.40 (t, 2H), 6.17-7.64 (m, 26H).



**Figure S1.** Integrated absorbance, as determined by EPR spectroscopy, versus DPPH concentration in toluene for 190  $\mu\text{L}$  of solution (black squares) and least squares linear fit (red line,  $y = 13851 + 1696070x$ ,  $r^2 = 0.999$ ).



**Figure S2.** Second and 3/2 order plots of UV-vis spectrophotometry-measured dark lophyl radical concentration decay for (a) *o*-Cl-HABI and (b) *p*-HOH-HABI at varying initial incident irradiation intensities (0.5 (black), 1.0 (red), 2.0 (blue), and 5.0 (green) mW·cm<sup>-2</sup>), and (c) *o*-Cl-HABI and (d) *p*-HOH-HABI at varying initial HABI concentrations (0.5 (black), 1.0 (red), 2.5 (blue), and 5.0 (green) mM). Experimental data and corresponding linear regression fits are shown as symbols and dashed lines, respectively. Error bars represent standard error for triplicate experiments. For clarity, not all experimental data points are plotted.

**Table S1.** 3/2 order *o*-Cl-HABI-derived lophyl radical recombination and first order *o*-Cl-HABI photodissociation rate constants for EPR spectroscopy-measured HABI photolysis in toluene solution under irradiation with 455 nm light and in the dark.

[HABI] <sub>0</sub> (mM)	<i>I</i> <sub>0</sub> (mW·cm <sup>-2</sup> )	<i>k</i> <sub>rec</sub> (mM <sup>-0.5</sup> ·sec <sup>-1</sup> )	<i>k</i> <sub>dis</sub> (sec <sup>-1</sup> )
5.0	0.5	4.68 × 10 <sup>-2</sup>	0.56 × 10 <sup>-4</sup>
	1.0	4.21 × 10 <sup>-2</sup>	0.90 × 10 <sup>-4</sup>
	2.0	3.75 × 10 <sup>-2</sup>	1.64 × 10 <sup>-4</sup>
	5.0	3.28 × 10 <sup>-2</sup>	2.99 × 10 <sup>-4</sup>
0.5	5.0	3.89 × 10 <sup>-2</sup>	5.49 × 10 <sup>-4</sup>
1.0		3.40 × 10 <sup>-2</sup>	4.62 × 10 <sup>-4</sup>
2.5		3.23 × 10 <sup>-2</sup>	3.31 × 10 <sup>-4</sup>
5.0		3.17 × 10 <sup>-2</sup>	2.95 × 10 <sup>-4</sup>