

Supporting Information

Near-Infrared Chemiluminescence up to 1700 Nanometers from Narrow-Bandgap Compounds and Polymers

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Materials and Methods

Materials

Oxalyl chloride (ReagentPlus, 99%) was ordered from Sigma-Aldrich company. Hydrogen peroxide (~35%) was obtained from commercial source without purification. Solvents for the emission test were dried and freshly distilled. Small compounds **1-4**¹ and polymer **5**² were prepared as previously described.

Methods

Absorption and fluorescence spectra were recorded with Shimadzu UV-3600 spectrophotometer and PTI fluorescence system, respectively. Near infrared chemiluminescence was studied by PTI fluorescence system with a germanium detector. The excitation source was turned off and the chemiluminescence signal was modulated by placing a chopper between the reaction cell and the detector and the signal was recorded by timebase mode. The light measurement was carried out by combining appropriate solutions of fluorescent dyes, hydrogen peroxide and oxalyl chloride in THF.

Solution emission quantum yields were measured by the method described in reference.³ A number of diluted solutions of different dye concentrations ($A < 0.1$, to prevent reabsorption) were prepared and the absorbance (A) and the integrated fluorescence intensity (D) at each concentration were recorded at a given excitation wavelengths (excitations for **1**, **2** and **5** are at their maximum absorption wavelengths; for **3** and **4** are at 980 nm). Then a graph of D versus A was plotted to determine the gradient (G). Quantum yields (Φ) were calculated using the following equation:

$$\Phi_s = \Phi_r \left(\frac{G_s}{G_r} \right) \left(\frac{I(\lambda_r)}{I(\lambda_s)} \right) \left(\frac{n_s}{n_r} \right)^2$$

The subscripts r and s refer to the reference dye and the sample, respectively. n is the refractive index of the solvent. $I(\lambda)$ is the relative intensity of the exciting light at wavelength λ . IR-125 was used as reference dye ($\Phi = 0.13$ in DMSO).⁴

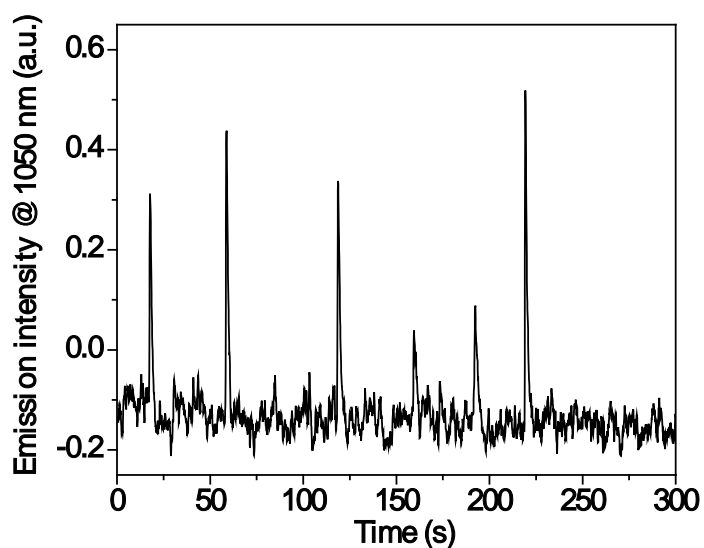


Figure S1. Flash CL emission at 1050 nm from compound **2** and hydrogen peroxide in THF upon addition of oxalyl chloride at intervals. Conditions: compound **2** (10^{-5} M) and hydrogen peroxide (3×10^{-5} M) in THF (3 mL). Oxalyl chloride (10^{-7} mmol) was added each time.

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