

Supporting Information

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Tailoring Intermolecular Interactions for Efficient Room-Temperature Phosphorescence from Purely Organic Materials in Amorphous Polymer Matrices**

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General experimental procedures

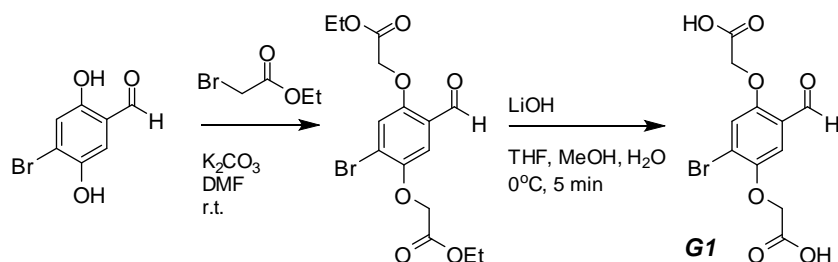
Synthetic details. iPMMMA (Aldrich, $M_w = 120,000$ g/mol), PVA80 (Aldrich, $M_w = 9,000 - 10,000$ g/mol), PVA100 (Aldrich, $M_w = 89,000 - 98,000$ g/mol), and PVAc (Aldrich, $M_n = 167,000$ g/mol) were used as polymer matrix without further purification. Br6A was synthesized following previously reported synthetic routes.¹ G1 and G2 were synthesized according to the procedure shown in Scheme S1 and Scheme S2, respectively. All chemicals purchases commercially, and used without further purification. The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into vanillin solution (9.0 g of vanillin and 1.5 mL of concentrated sulfuric acid in 300 mL of MeOH) and $KMnO_4$ solution (3 g of $KMnO_4$, 20 g of K_2CO_3 , and 5 mL of 5% NaOH solution in 300 mL of water). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60). Unless otherwise specified, all reactions were conducted under a slight positive pressure of dry nitrogen. The usual work-up refers to washing the quenched reaction mixture with brine, drying the organic extracts over anhydrous $MgSO_4$ and evaporating under reduced pressure using a rotary evaporator.

Spectroscopic Characterization. 1H -NMR spectrum was recorded on a Varian, MR 400 (400 MHz) in DMSO solution. ^{13}C -NMR spectrum was recorded on a Varian, MR400 (400 MHz) in DMSO solution. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard, and coupling constants in Hertz. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray in positive ion detection (ESI+) mode. Significant fragments are reported in the following fashion: m/z (relative intensity). Elemental analysis was carried out using a CE instruments, EA1110 elemental analyzer. UV-visible absorption spectra were measured on a Varian Cary50 UV/Vis spectrophotometer. Photoluminescence, Absolute quantum yield and Time-resolved fluorescence lifetime were obtained using a Photon Technologies International (PTI) Quanta master TM spectrofluorometers equipped with an integrating sphere and a laser excitation system. The relative fluorescence quantum yield was measured using Rhodamin B in Ethanol as a standard reference (1×10^{-7} mol L^{-1} , $\Phi_F=95\%$). Absorption and emission inside the sphere were determined by comparison to a blank sample (glass only). A neutral density filter was used to allow for maximization of the emission signal without saturating the photomultiplier tube detector with excitation light. Each sample type was run in quadruplicate with each quantum yield measurement coming from a freshly drop cast sample. Measurements proved highly repeatable, and errors are given as ± 1 standard deviation.

Reference

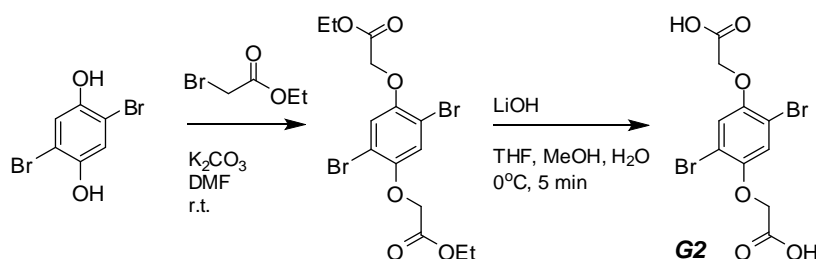
1. Bolton, O.; Lee, K.; Kim, H. J.; Lin, K. Y.; Kim, J. *Nat. Chem.* **2011**, *3*, 205–210.

Synthesis



Scheme S1. The synthetic scheme of **G1**

2,2'-(2-bromo-5-formyl-1,4-phenylene)bis(oxy)diacetic acid (G1). To a solution of diethyl 2,2'-(2-bromo-5-formyl-1,4-phenylene)bis(oxy)diacetate (200 mg, 0.52 mmol) in THF (2.4 ml) and methanol (1.2 ml) was added lithium hydroxyde (38 mg, 0.780 mmol) dissolved in water (2.4 ml) at 0°C . The solution was stirred at 0°C for 4 hrs and then poured into 1 M HCl (aq). The resulting white precipitates were filtered and washed with water and methanol (158 mg, 92 %). ^1H NMR (400 MHz, DMSO-d_6): δ 10.34 (s, 1 H), 7.58 (s, 1 H), 7.16 (s, 1 H), 4.90 (s, 2H), 4.82 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 188.4, 169.9, 169.7, 154.7, 149.0, 124.2, 120.0, 119.4, 110.0, 66.0, 65.6. MS m/z (EI, relative intensity): 332 (M^+ , 3), 288 (4), 241 (2), 252 (69), 229 (14), 215 (87), 192 (52), 178 (32), 165 (99), 149 (67), 137 (69), 121 (25), 107 (44), 93 (14), 80 (100), 65 (21). HRMS (EI) calcd. for $\text{C}_{11}\text{H}_9\text{BrO}_7$ (M^+) 331.9531, found 331.9533.



Scheme S2. The synthetic scheme of **G2**

2,2'-(2,5-dibromo-1,4-phenylene)bis(oxy)diacetic acid (G2). To a solution of diethyl 2,2'-(2,5-dibromo-1,4-phenylene)bis(oxy)diacetate (200 mg, 0.455 mmol) in THF (1.8 ml) and methanol (0.9 ml) was added lithium hydroxyde (33 mg, 1.36 mmol) dissolved in water (1.8 ml) at 0°C . The solution was stirred at 0°C for 8 hrs and then poured into 1 M HCl (aq). The resulting white precipitates were filtered and washed with water and methanol (160 mg, 86 %). ^1H NMR (400 MHz, DMSO-d_6): δ 13.10 (s, 2 H), 7.28 (s, 2 H), 4.79 (s, 4 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.8, 148.9, 118.0, 110.0, 65.8. MS m/z (EI, relative intensity): 410 (M^+ , 16), 384 (1), 353 (7), 333 (31), 283 (5), 266 (16), 229 (3), 201 (6), 159 (2), 125 (3), 97 (9), 73 (63), 58 (44). HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{12}\text{Br}_2\text{O}_6$ (M^+) 409.9001, found 409.8996.

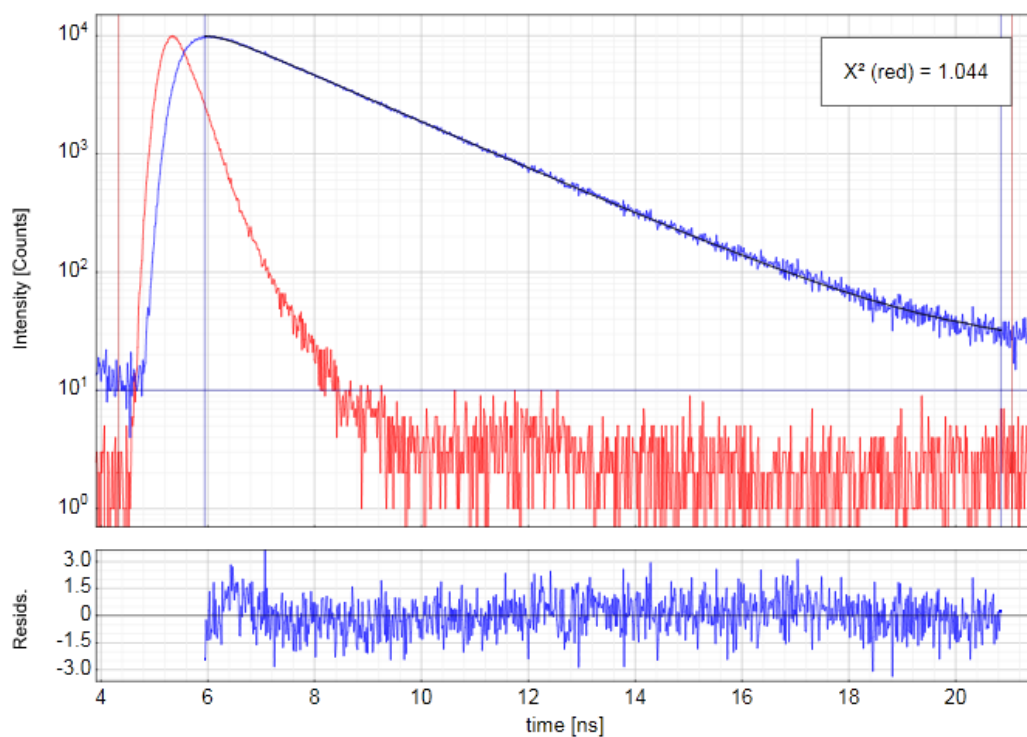


Figure S1 Fluorescence decay profiles (upper blue lines) of **G1** solution (H₂O, 1×10^{-5} M) with 377 nm excitation. IRFs are represented in red, fits in black; lower blue lines are the residuals.

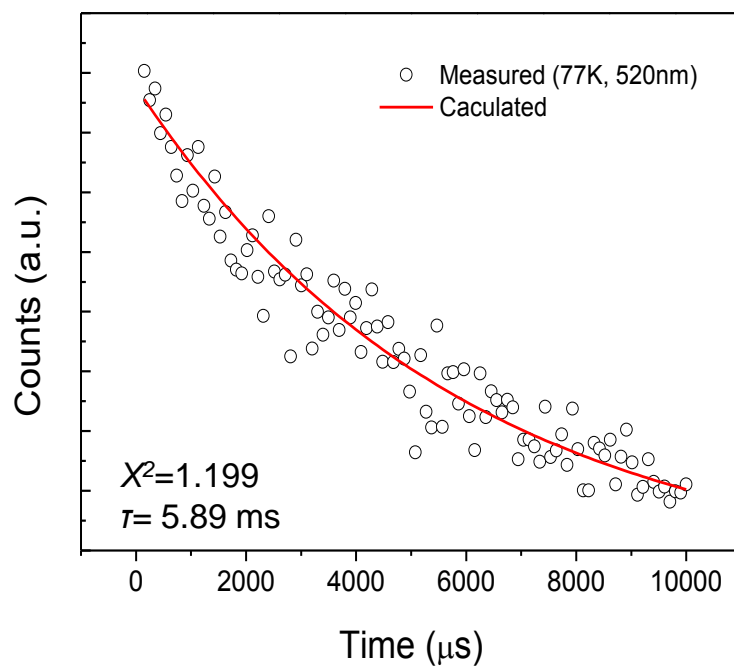


Figure S2 Time-resolved measurement of 530 nm emission from **G1** solution (H_2O , 1×10^{-5} M) at 77K with fit to long-lived component. Lifetime and X^2 are indicated.

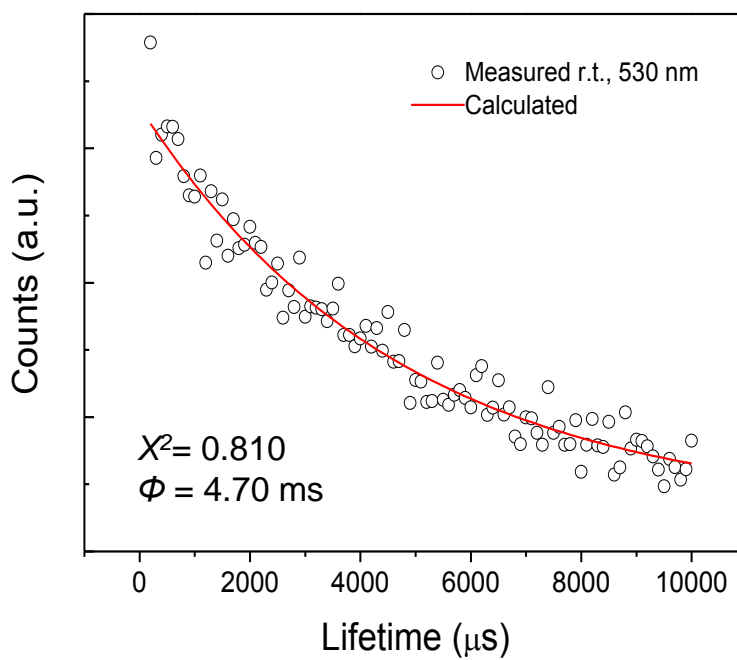


Figure S3 Time-resolved measurement of 530 nm emission from **G1-PVA** thin film (1wt% G1 versus 80% hydrolyzed PVA) with fit to long-lived component. Lifetime and X^2 are indicated.

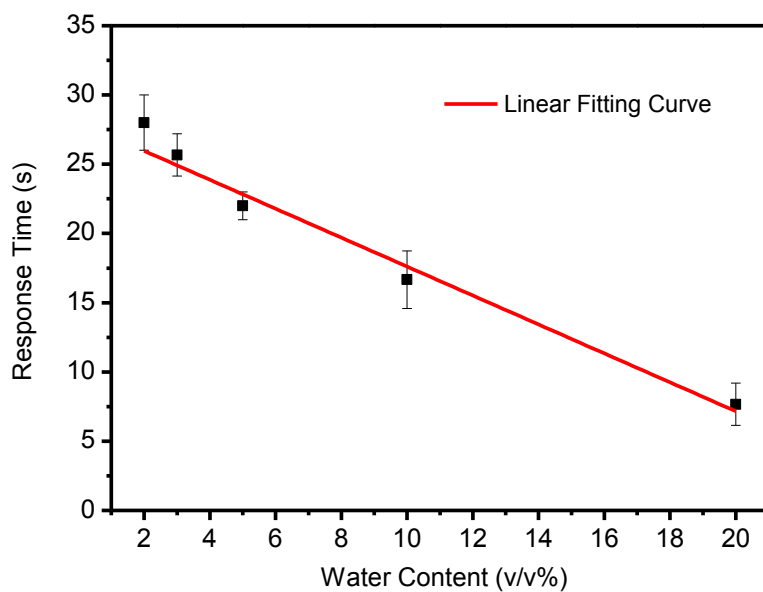


Figure S4. Correlation curve of water content in gasoline versus response time for water-in-fuel sensing application

Our phosphorescence system can be also used as a water indicator to in fuel or organic solvents. It is well known that fuel injector inside the automobile engine is easily damaged by presence of water. We investigated the correlation between the ‘phosphorescence to fluorescence’ switching time of G1-PVA100 thin films (10wt% G1) and the water content in commercial gasoline. As the amount of water in gasoline increases, the response time decreases linearly as shown in **Figure S4**, allowing quantitative analysis. Because the prepared G1-PVA100 thin films respond not to other organic solvents but to only water they can be used as a water indicator in organic solvents as well.

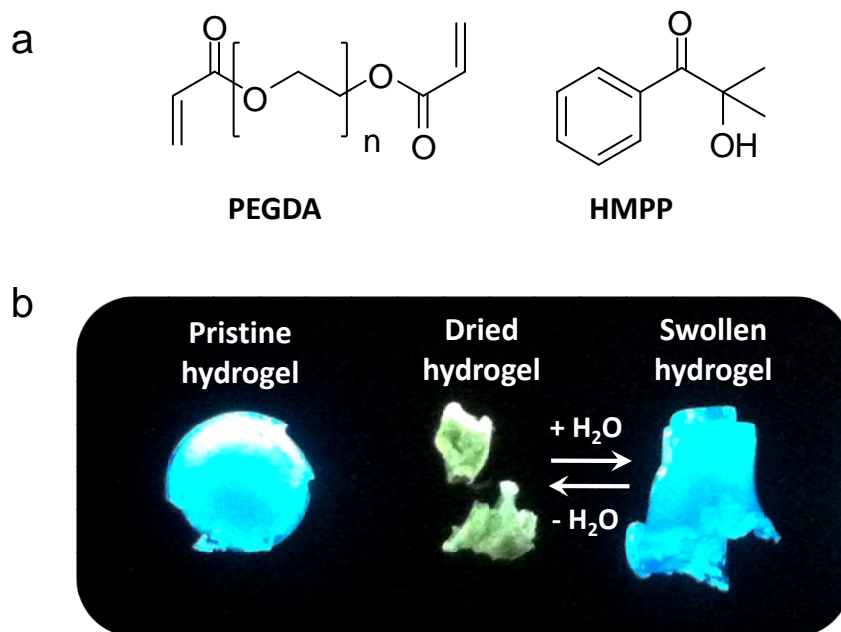


Figure S5. (a) Chemical structures of PEGDA and HMPP (b) Photoluminescence images of G1-PVA80 embedded hydrogel.

Residual water monitoring is an important procedure during root canal treatment in dentistry and thus a simple water sensing kit would provide great convenience. We constructed phosphorescence hydrogel prepared by UV-polymerization of an aqueous solution of G1-PVA80 (10 wt% G1 relative to PVA80), polyethylene glycol diacrylate (PEGDA), and 2-hydroxy-2-methylpropiophenone (HMPP) (see **Figure S5a**). In this formulation, PEGDA was used as a monomer and HMPP was employed as a photoinitiator for making hydrogel with PVA80. Pristine hydrogel bearing water emitted strong blue fluorescence. However, once the gel was dried completely it showed green phosphorescence (**Figure S5b**). The hydrogel was readily swollen by small amount of water and subsequently changed the emission color from green phosphorescence to blue fluorescence.