Multi-luminescent Switching of Metal-Free Organic Phosphors for Luminometric Detection of Organic Solvents

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Methods

1. Sample preparations

1.1. Chemicals

Unless otherwise specified, all chemicals were purchased commercially, and used without further purification. Isotactic poly (methyl methacrylate) (iPMMA, M_w = 120,000 g/mol, Aldrich), poly (vinyl alcohol) (PVA80, M_w = 9,000 – 10,000 g/mol, 80% hydrolyzed, Aldrich), and poly (vinyl alcohol) (PVA100, M_w = 89,000 – 98,000 g/mol, 99+% hydrolyzed, Aldrich) were used without further purification. Br6A and G1 were synthesized following previously reported synthetic routes.[1,2]

1.2. Preparation of electrospun fiber mats of Br6A-iPMMA, G1-PVA80, and G1-PVA100

Electrospun fiber mats were fabricated from three different polymer solutions: (1) 4 w/v% iPMMA in dichloromethane (DCM) with a 1 w/w iPMMA% addition of organic phosphor, Br6A; (2) 35 w/v%

PVA80 in distilled water with a 1 w/w PVA80% addition of organic phosphor, G1; (3) 10 w/v% PVA100 in water with a 1 w/w PVA100% addition of organic phosphor, G1. Polymer solution 1 was pumped at 0.45 mL/hr through a 26G needle charged to 6-7 kV. Polymer solution 2 was pumped at 0.15 mL/hr through a 26G needle charged to 15 kV. Polymer solution 3 was pumped at 0.15 mL/hrthrough a 26G needle charged to 21 kV. All resultant fibers were collected on a high speed rotating drum collector (NanoNC, Korea) spinning at 1000 rpm (4.5 m/s) located 15 cm below the capillary tip.

2. Sample measurements

UV-visible absorption spectra were measured on a Varian Cary50 UV/Vis spectrophotometer. Photoluminescence spectra were obtained using a Photon Technologies International (PTI) QuantaMaster spectrofluorometer.

3. Supplementary references

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

2. M. S. Kwon, D. Lee, S. Seo, J. Jung, *Angew. Chem. Int. Ed.* **2014**, 53, 11177

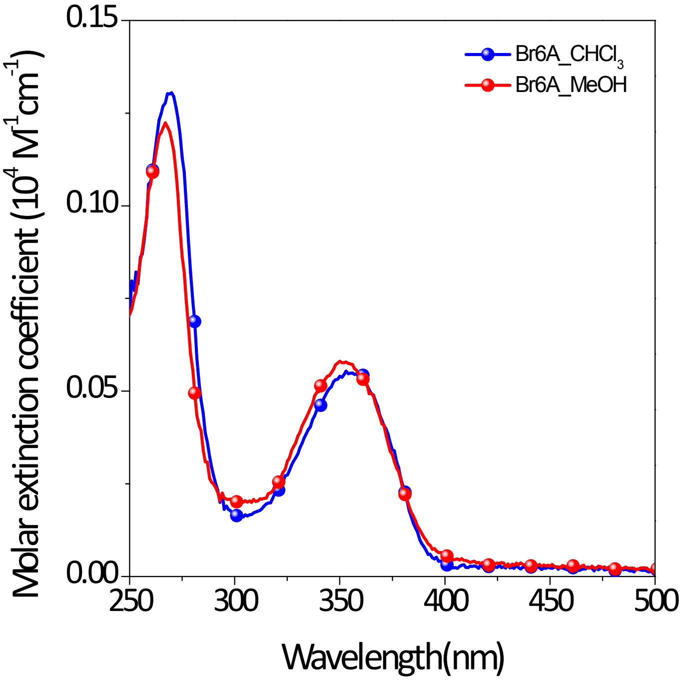

Figure S1. UV-Vis spectra of chloroform (blue line) and methanol (red line) solution of Br6A

Table S1. Phosphorescence properties of phosphors-doped polymer films[a]

sample[b]	conditions	Φ_P (%)[c]	τ_P (ms)[c,d]
Br6A-doepd *i*PMMA	under air R.T.	7.0 (0.60)	1.90 (0.06)
G1-doped PVA80	under air R.T.	21.0 (0.59)	5.84 (0.42)
G1-doped PVA100	under air R.T.	26.5 (1.03)	6.66 (0.64)

[a]We measured quantum efficiency (Φ_P) and phosphorescence lifetime (τ_P) of the drop-cast phosphor-doped polymer films. [b]The phosphor-doped drop-casted polymers were prepared by following procedures;1.0 wt% of iPMMA, PVA80, and PVA100 were dissolved in chloroform ($CHCl_3$) or distilled water mixed with the phosphor (1.0 wt% of Br6A or G1 for polymers, respectively). The mixed solutions were drop-cast on a pre-cleaned glass substrate and kept at RT for 10 minutes. The resulting drop-cast films were thermally annealed at 120°C for 20 minutes and kept in a vacuum chamber for 30 minutes to completely remove residual solvent. All processes from drop-cast to packaging were done in a nitrogen filled glove box. The measurements of the resulting samples were carried out under air at R.T. [c]Preparation of the polymer films and measurements are fully optimized so that the results are somewhat different from previously published data.[1,2] [d]Phosphorescence lifetimes were obtained by fitting only the long-component of phosphorescence profiles through a mono-exponential function.

Table S2. TD-DFT calculated singlet and triplet states of Br6A: energy (E), oscillator strength (*f*), configuration interaction (CI) description (H = HOMO, L= LUMO)

solvent	state	E / eV (λ / nm)	*f*	main CI configuration	nature
Vacuum	T_1	2.76 (450)		H→L (94%)	ππ*
	T_2	3.15 (394)		H-1→L (92%)	nπ*
	T_3	3.49 (355)		H-2→L (71%)	ππ*
	S_1	3.66 (339)	0.00	H-1→L (96%)	nπ*
	S_2	3.77 (329)	0.13	H→L (94%)	ππ*
MeOH	T_1	2.68 (463)		H→L (96%)	ππ*
	T_2	3.28 (378)		H-2→L (93%)	nπ*
	T_3	3.45 (359)		H-1→L (33%)	ππ*
	S_1	3.61 (343)	0.16	H→L (96%)	ππ*

	S_2	3.78 (328)	0.00	H-2→L (96%)	nπ*