

Electronic Supplementary Information

Switching the emission of tetrakis(4-methoxyphenyl)ethylene among three colors in solid state

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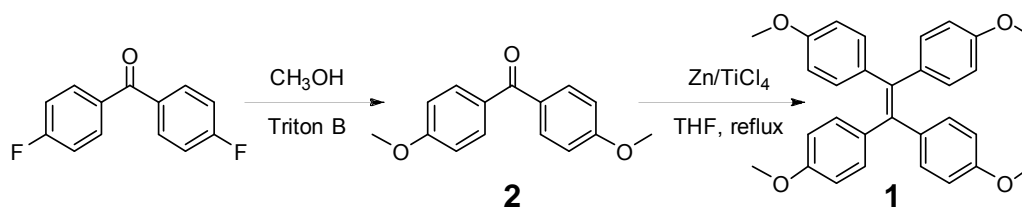
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Materials and Instrumentations

4,4'-dihydroxybenzophenone, bis(4-fluorophenyl)methanone were purchased from Alfa Aesar. Potassium carbonate, titanium tetrachloride, zinc dust, 1-bromoethane, acetone, methanol, ammonium chloride, Triton B (C₁₀H₁₆NOH) and anhydrous magnesium sulfate were purchased from Sinopharm Chemical Reagent Co., Ltd. THF was purchased from Aldrich and distilled under normal pressure from sodium benzophenone ketyl under argon immediately prior to use.

All the reactions were carried out under a nitrogen atmosphere using Schlenk technique. ¹H and ¹³C NMR spectra were recorded using a Bruker AV 400 Spectrometer at 400 and 100 MHz in DMSO-d₆ solutions, respectively. Tetramethylsilane was used as the internal standard. An LCT Premier XE time-of-flight mass spectrometer (Micromass), equipped with a dual sprayer orthogonal electrospray source (LockSpray), was used to obtain exact mass measurements. Fluorescence spectra of all samples were measured by a Cary Eclipse spectrofluorometer. Infra-red (IR) spectra were obtained on a Nicolet Fourier spectrofluorometer. Differential scanning calorimetry (DSC) was carried out using a Mettler DSC 1 instrument at a scanning rate of 10 K min⁻¹. Powder X-Ray diffraction (XRD) patterns were performed on an X'Pert PRO MPD diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 25 °C (scan range: 4.5-50°). Single crystals data was collected on a Bruker Smart APEXII CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda=0.71070 \text{ \AA}$). Melting points were measured by DSC analysis. All photographs were recorded on a FinePix S7000 digital camera. The thermal annealing processes were carried out in oven. The amorphous solid of luminogens were prepared by heating the luminogens to melt with a heating gun and quenching the melt with liquid nitrogen.

Synthesis of luminogen **1**



Compound **2** was synthesized according to the procedure described in the previous literature.^[1]

Compound **1** was synthesized by a typical self-McMurry coupling reaction. A 250-mL two-necked flask equipped with a magnetic stirrer was charged with zinc dust (3.3 g, 50 mmol) and 60 mL THF under nitrogen atmosphere. The mixture was cooled to 0 °C, and TiCl_4 (2.75 mL, 25 mmol) was added slowly by a syringe. The mixture was refluxed for 2.5h and cooled to 0 °C. The raw material **2** (4.8g, 20 mmol) in THF (60 mL) was added to the mixture. Then the mixture was refluxed until TLC showing complete conversion. The reaction was quenched with saturated aqueous NH_4Cl solution, and extracted with diethyl ether. The organic layer was desiccated with anhydrous magnesium sulfate for two hours, and then filtered. The solvent were removed by evaporation. Finally the resulting residue was purified by recrystallization from acetone to give white powder **1** (3.5g, 75%). M.p. 181-182 °C. ^1H NMR (DMSO- d_6 , 400MHz) δ =3.67 (s, 12H, OCH_3), 6.67-6.69 (d, 8H, Ar-H), 6.84-6.86 (d, 8H, Ar-H). ^{13}C NMR (100MHz, DMSO- d_6 , δ):157.38, 137.94, 136.18, 131.88, 113.11, 54.81. IR: 2832, 1604, 1509, 1455, 1296, 1239, 1167, 1032, 832. HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{28}\text{O}_4$ $[\text{M} + \text{H}]^+$: 453.2060; found, 453.2073.

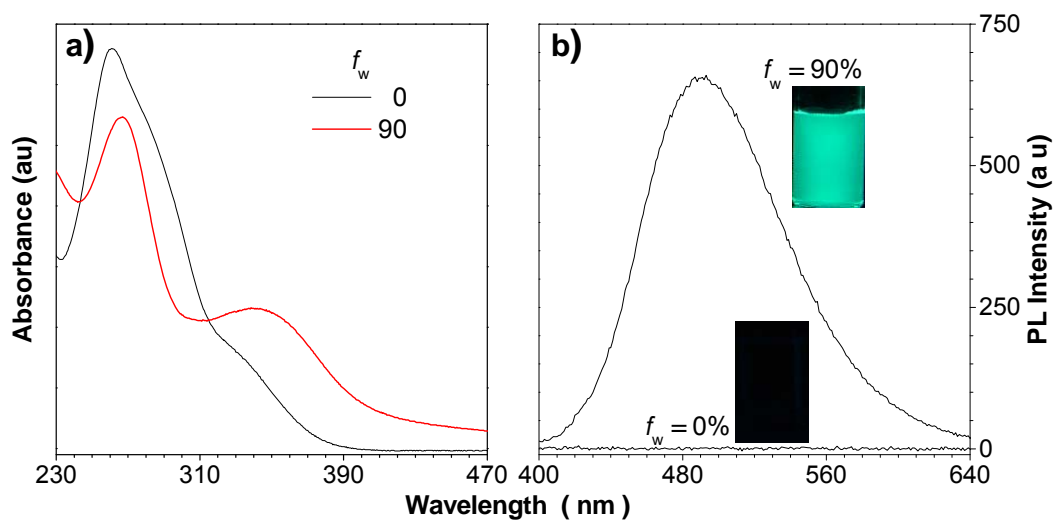


Fig. S1 UV and PL spectra of luminogen **1** in acetonitrile/water mixtures with 0 and 90% water fraction (f_w). Concentration: 10 μ M. Photos were taken under 365 nm UV illumination.

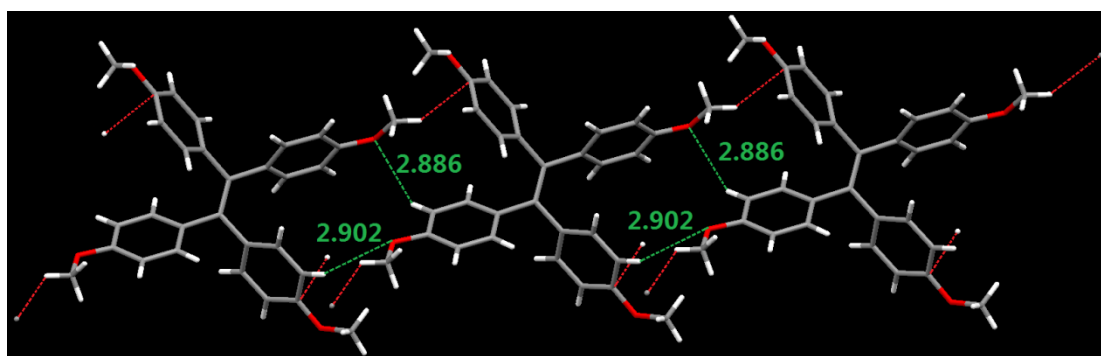


Fig. S2 View of C-H... π (red dashed line, the distance is 2.768 Å) and C-H...O (green dashed line, the distances are 2.886 and 2.902 Å) between molecules in single crystal of **1** (1CA).

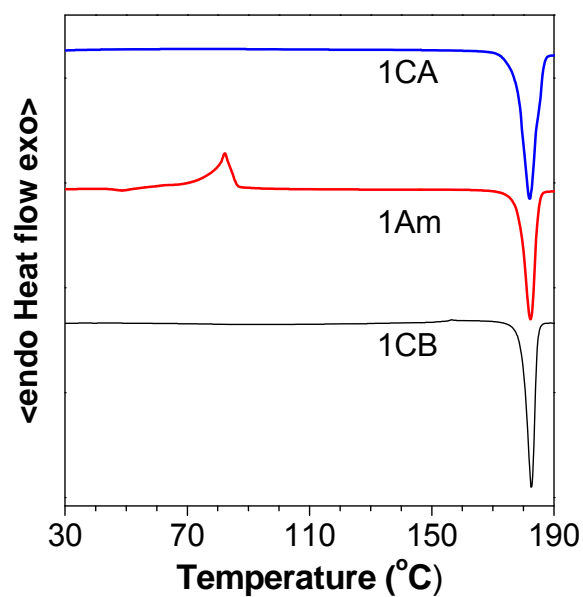


Fig. S3 DSC thermograms of luminogen 1.

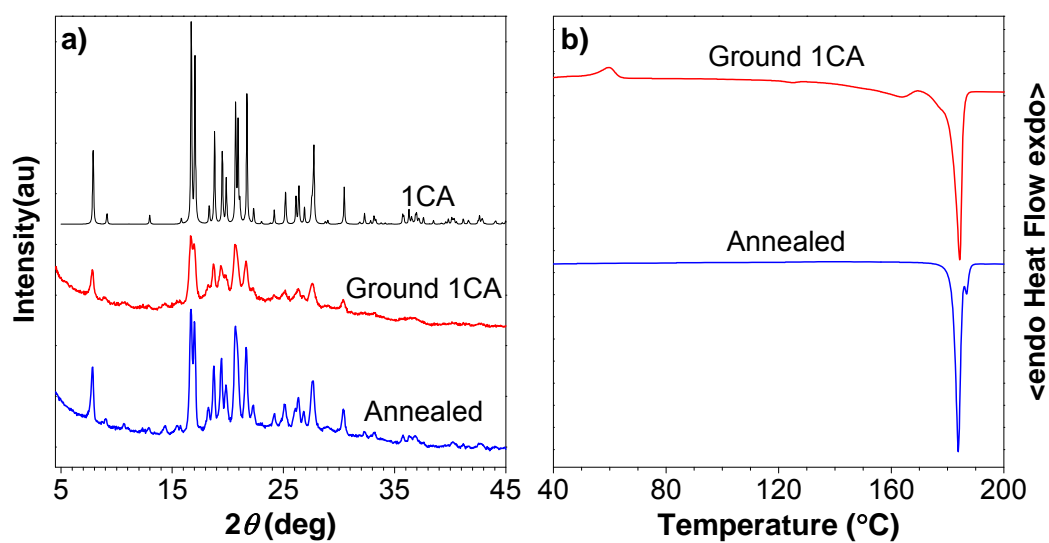


Fig. S4 a) Powder XRD patterns and b) DSC thermograms of luminogen 1 in different aggregate states.

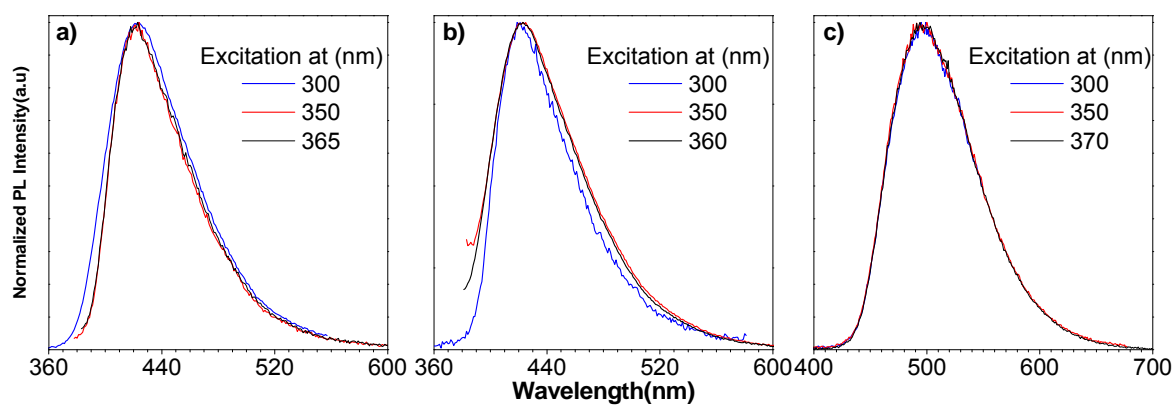


Fig. S5 PL spectra of a) 1CA, b) ground 1CA after annealing, and c) 1Am excited at different wavelength.

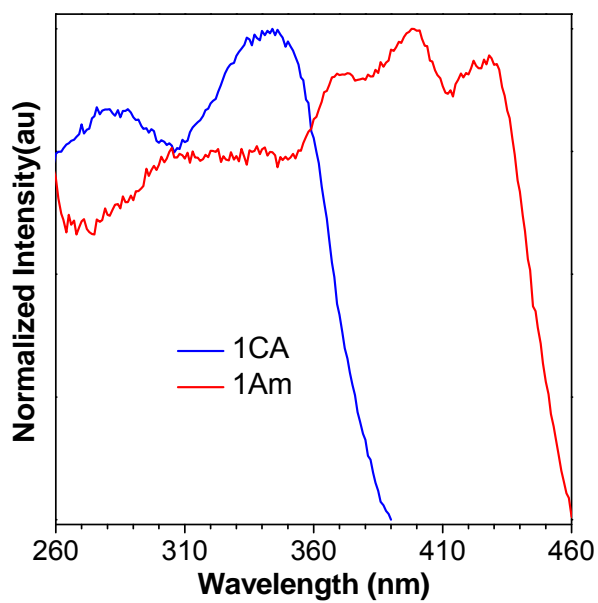


Fig. S6 Excitation spectra of 1CA and 1Am.

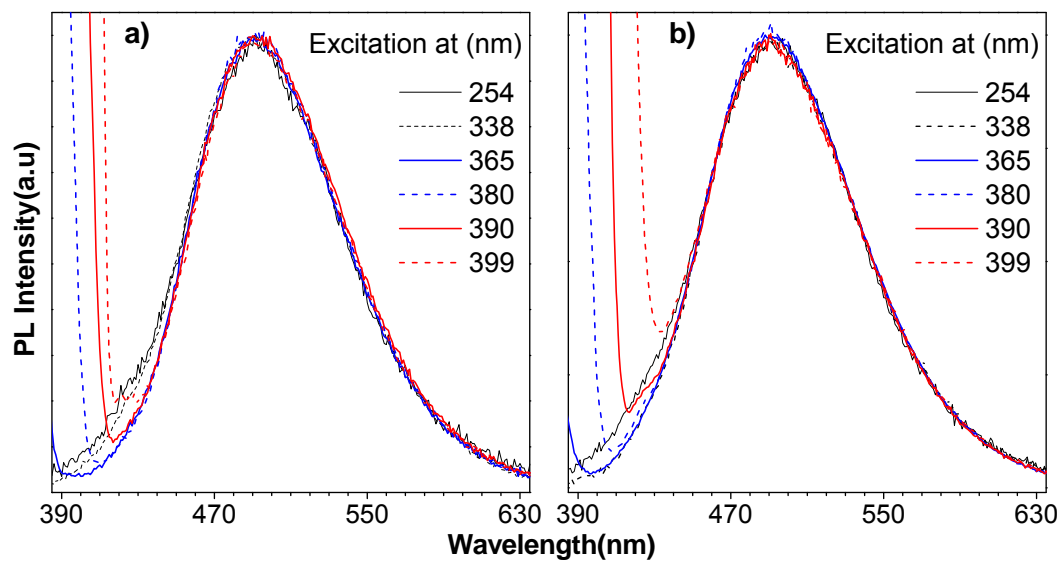


Fig. S7 PL spectra of ground sample from a) 1CA and b) 1CB excited at different wavelength.

Samples were prepared by shearing a tip of crystal on the inner wall of quartz cell.

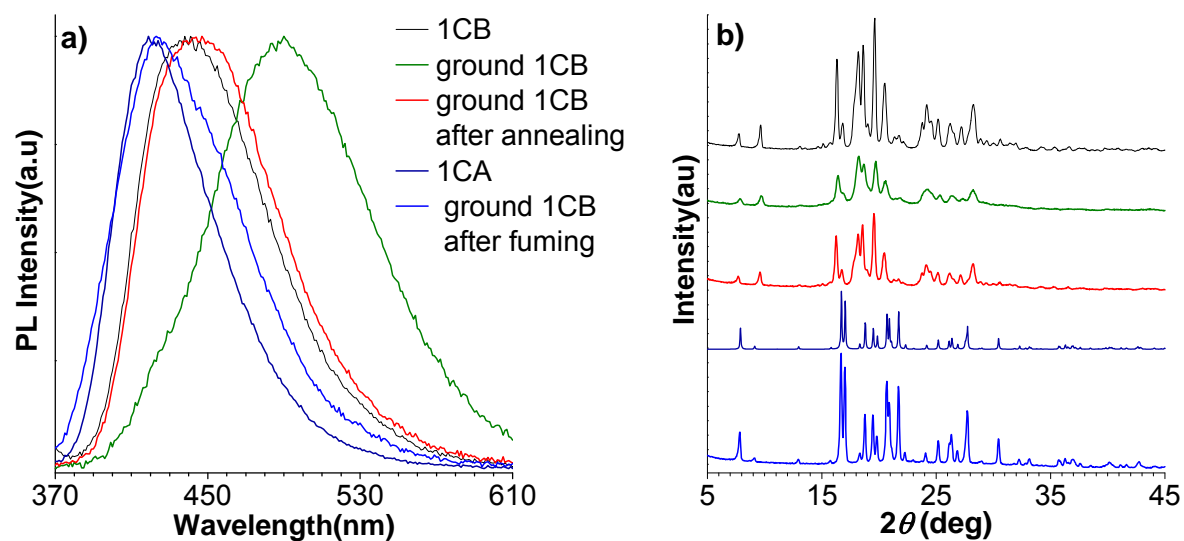


Fig. S8 a) PL spectra and b) powder XRD patterns of ground solid from 1CB before and after annealing or fuming. Curve of 1CB and 1CA are provided for comparison.

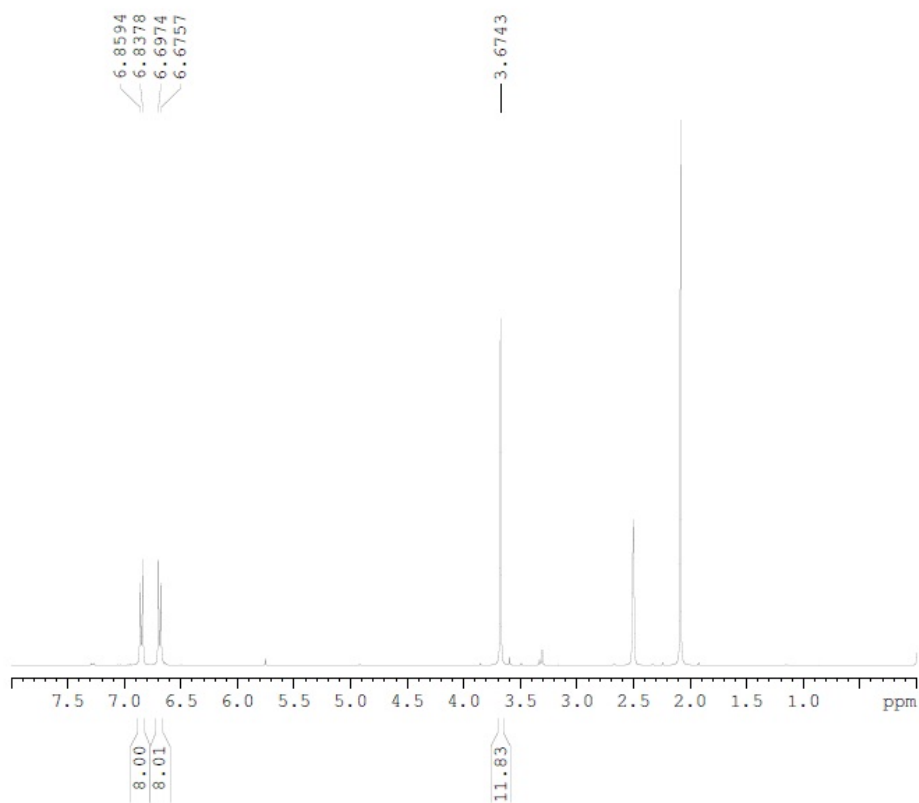


Fig. S9 The ^1H NMR spectrum of **1** in DMSO- d_6 solution.

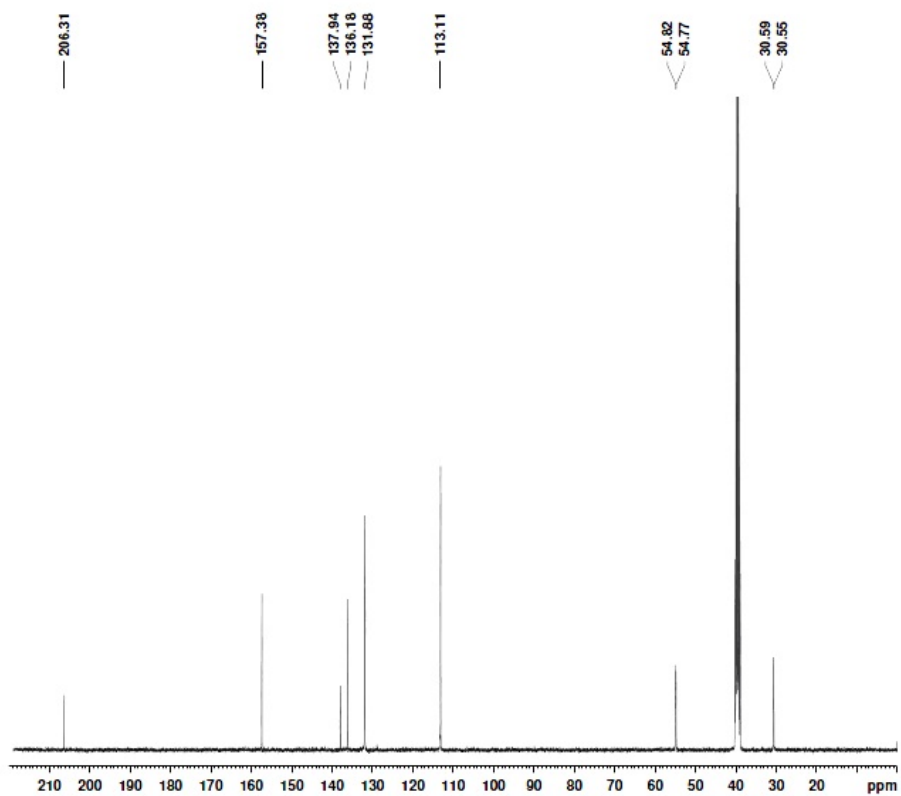


Fig. S10 The ^{13}C NMR spectrum of **1** in DMSO- d_6 solution.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

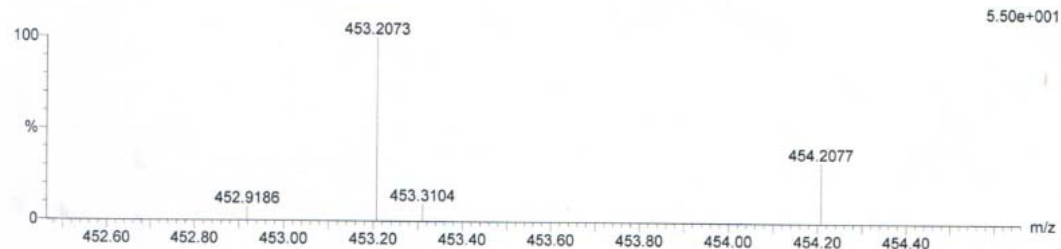
608 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-50 H: 0-80 N: 0-10 O: 0-10

LXL110509-1 10 (0.185)

TOF MS ES+



Minimum:									
Maximum:		10.0	5.0	-1.5					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula			
453.2073	453.2079	-0.6	-1.3	21.5	n/a	C31	H25	N4	
	453.2066	0.7	1.5	16.5	n/a	C30	H29	O4	
	453.2057	1.6	3.5	4.5	n/a	C14	H29	N8	O9

Fig. S11 The HRMS spectrum of compound 1.

References

- [1] H. M. Meshram, P. R. Goud, B. C. Reddy, and D. A. Kumar. *Synthetic Communications*, 2010, 40: 2122–2129.