Electronic Supplementary Information （ESI）

A unique dansyl-based chromogenic chemosensor for rapid and ultrasensitive hydrazine detection

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Contents

1. Determination of fluorescence quantum yield [S1]

The quantum yield (Φ) was calculated using the following equation [1]

$$\Phi_x = \Phi_s (F_x/F_s) (A_s/A_x) (n_{x2}/n_{s2}),$$

where, X and S indicate the unknown and standard solution respectively, Φ = quantum yield, F = area under the emission curve, A = absorbance at the excitation

wavelength and n = index of refraction of the solvent. Φ measurements were performed using fluorescein in 0.1 N sodium hydroxide as standard (Φ = 0.85). Using this equation, we calculated the Φ of the solution in the absence and presence of hydrazine to be 0.093 and 0.498, respectively. The remarkably increase of the Φ may be due to the fine optical properties of dansyl fluorophore.

2. Calculation of the detection limit [S2]

The detection limit (DL) of **DPI** for hydrazine was determined as follows [2]:

$$DL = K \times Sb1/S,$$

where K = 3, Sb1 is the standard deviation of the blank solution and S is the slope of the calibration curve. From the formula and calibration curve constructed for the determination of hydrazine, we get DL = 1.88×10^{-7} M for emission and 1.9×10^{-6} μM for absorbance, respectively. Under the optimal condition (5 μM probe for emission and 100 μM for absorbance, DMSO/H_2O = 9/1, 1 h reaction time, excitation/emission at 353 nm/512 nm at room temperature), the linear range for emission and absorbance were 0 - 5.0 μM (R^2 = 0.9911, n = 10) and 0 - 100 μM (R^2 = 0.9991, n = 10), respectively. Note that fluorescent DL (6.01 ppb) is much lower than the TLV (10 ppb) set by the EPA.

The detection limit based on IUPAC (CDL =3Sb/m) was calculated according to 10 blank measurements. The relationship between the absorbance ratio $A_{365\ nm}/A_{332\ nm}$ and hydrazine concentration is: $y = 1.036 \times 10^4 x + 0.77954$, where y is the

absorbance ratio $A_{365\ nm}/A_{332\ nm}$ and x is the $[N_2H_4]$. The relationship between the fluorescence intensity $I_{512\ nm}$ and $[N_2H_4]$ is: $y= 9.5 \times 10^7 x + 52.52$, where y is the fluorescence intensity at 512 nm and x is $[N_2H_4]$.

3. Table S1. Crystal data and structure refinement parameters of the DPI.

Formula	$C_{20}H_{16}N_2O_4S$	
Formula Weight	380.42	
Temperature (K)	293K	
Wavelength (Å)	0.71073	
Space group	Pbca	
Unit cell dimensions (Å, °)	a = 10.0878 (14) b = 12.7641 (16) c = 28.139 (4)	α = 90 β = 90 γ = 90
Volume (Å^3)	3623.2 (9)	
Calculated density, (g cm^{-3})	1.395	
F (000)	1584.0	
Goodness-of-fit on F^2	1.314	
R indices	R1 = 0.0448	wR2 = 0.1197

4. Supporting Figures:

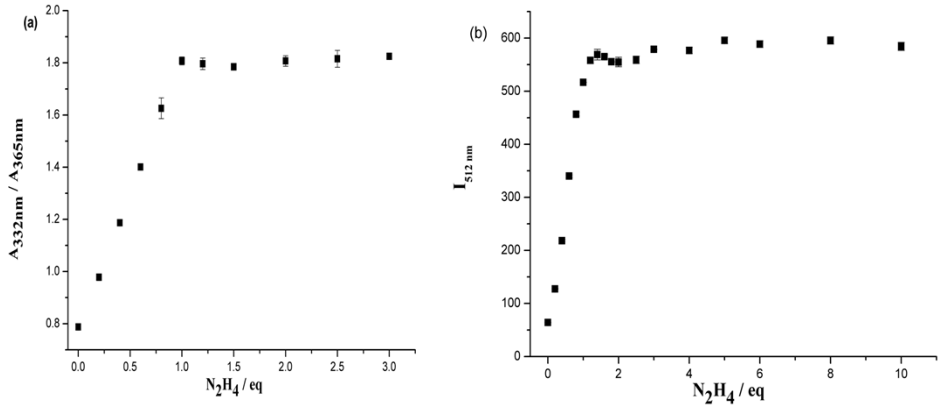

Figure S1. (a) Plot of absorption ratios at 332 nm and 365 nm ($A_{332\ nm}/A_{365\ nm}$) of **DPI** (100 μM) related to the equivalents of hydrazine (0 -3 eq) (b) Plot of emission intensity at 512 nm of **DPI** (5 μM) related to the equivalents of hydrazine (0 - 3 eq)

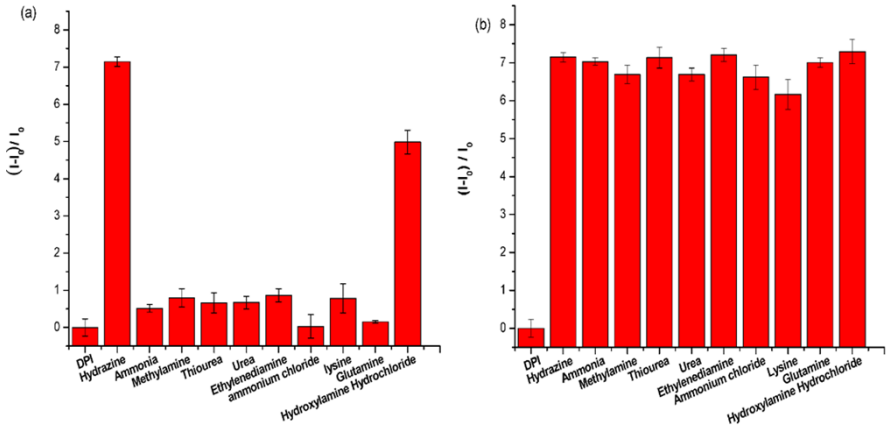

Figure S2. (a) The response of **DPI** (5 μM) in the presence of various analysts (25 μM). (λ_{ex} = 353 nm , λ_{em} = 512 nm) (b) The response of **DPI** (5 μM) in the presence of various amines (25 μM) and hydrazine (5 μM). (λ_{ex} = 353 nm , λ_{em} = 512 nm)

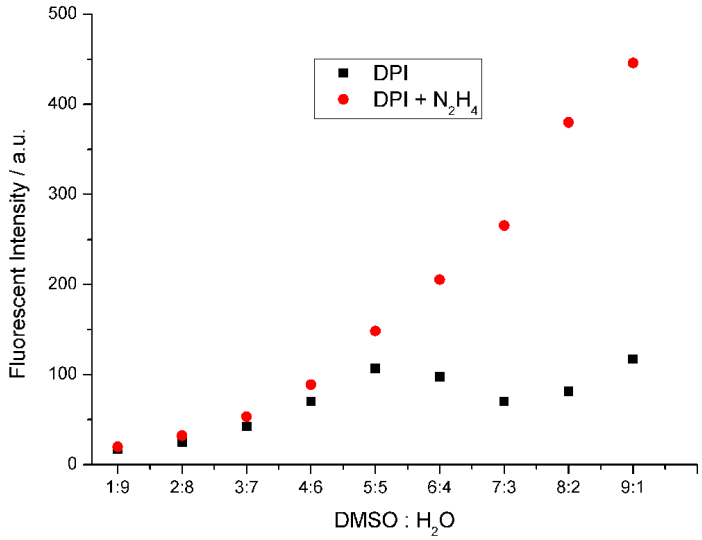

Figure S3. Solvent-dependent of **DPI** in the absence and presence of hydrazine. [**DPI**] = 5 μM, [N_2H_4] = 10 μM in a mixture of HEPES buffer (pH 7.0, 20 mM) and DMSO at rt. (λ_{ex} = 353 nm , λ_{em} (**DPI** + N_2H_4) = 512 nm, λ_{em} (**DPI**) = 475 nm)

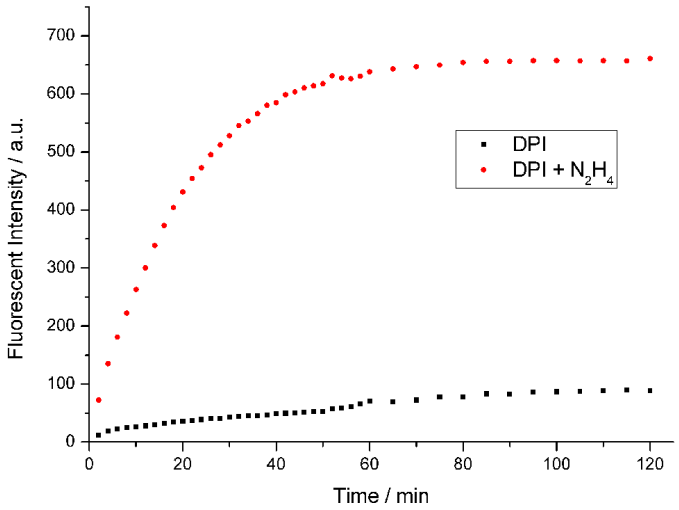

Figure S4. Time-dependent of probe **DPI** in the absence and presence of hydrazine. [**DPI**] = 5 μM, [N_2H_4] = 10 μM in a mixture of HEPES buffer (pH 7.0, 20 mM) and DMSO (1/9, v/v) at rt. (λ_{ex} = 353 nm , λ_{em} (**DPI** + N_2H_4) = 512 nm, λ_{em} (**DPI**) = 475 nm)

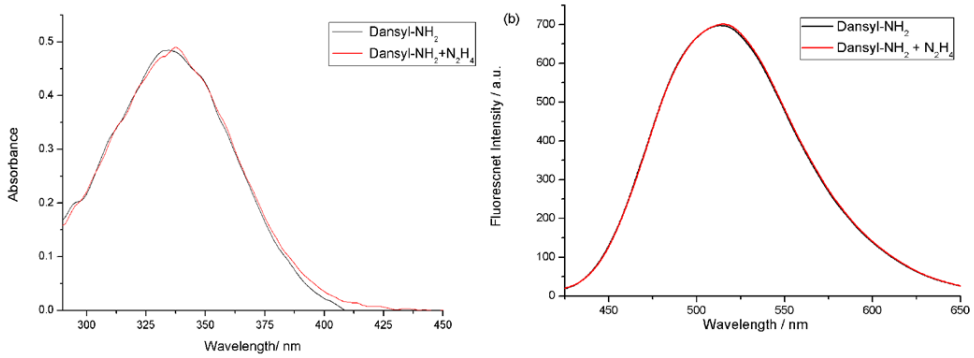

Figure S5. Absorbance (a) and Fluorescence emission spectra (b) of Dansyl-NH_2 in the absence and presence of hydrazine in a mixture of HEPES buffer (pH 7.0, 20 mM) and DMSO.

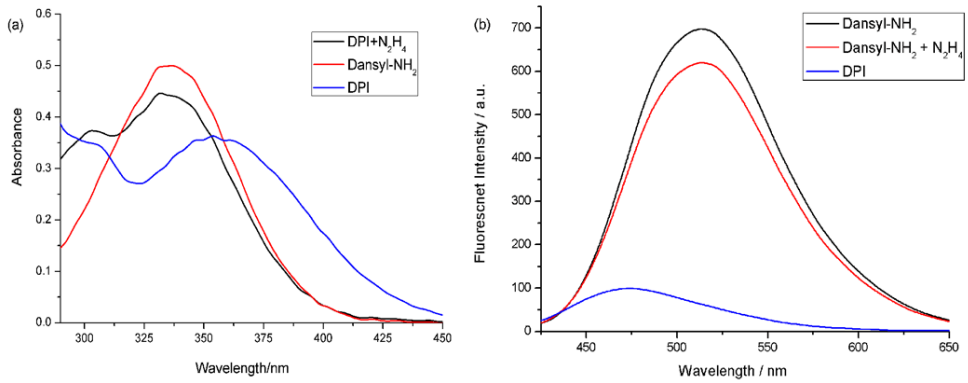

Figure S6. Absorbance (a) and Fluorescence emission spectra (b) of probe **DPI** in the absence and presence of hydrazine and Dansyl-NH_2 in a mixture of HEPES buffer (pH 7.0, 20 mM) and DMSO (1/9, v/v) at rt.

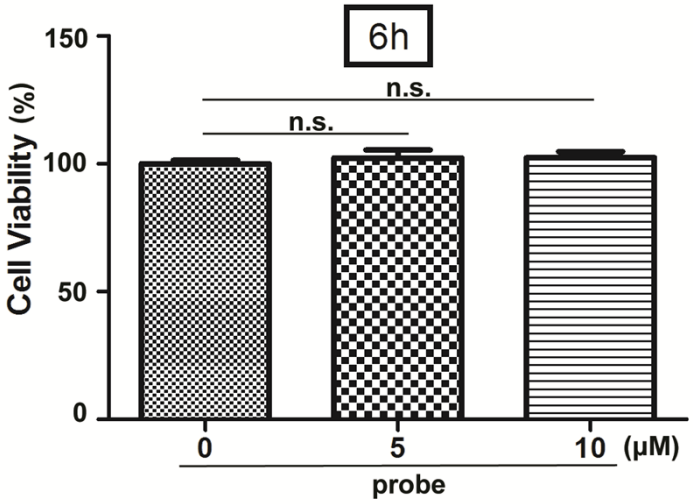

Figure S7. Cytotoxicity of **DPI** to HeLa cells. HeLa cells were incubated with 5 and 10 μM **DPI** for 6 h respectively. The cell viability was investigated by SRB assay.

5. Table S2. Determination of hydrazine in real samples by probe DPI.

Water Samples	Hydrazine Added (μM)	Found (μM)	Recovery (%)	RSD[a] (%)
Yellow Water	1.5	1.52	101.3	2.2
	2.5	2.34	93.6	2.0
	3.5	3.48	99.3	3.1
	4.5	4.51	100.2	3.0
Tap Water	1.5	1.47	98.0	1.5
	2.5	2.52	100.8	1.3
	3.5	3.55	101.4	2.2
	4.5	4.63	102.8	2.4

a: Relative Standard Deviation of 3 individual measurements.

6. Characterization data for DPI

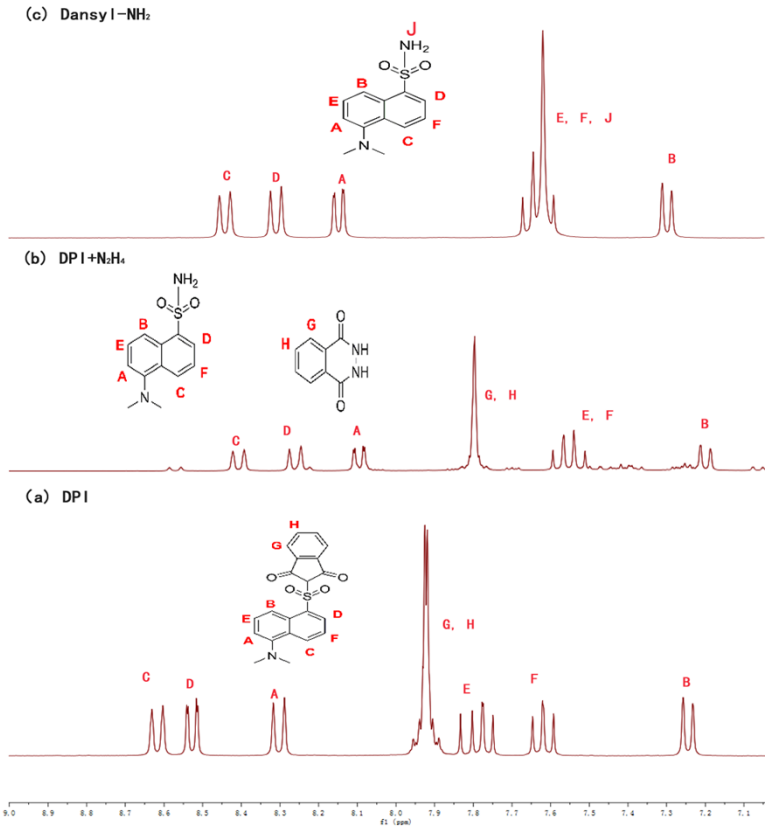

Figure S8. ^{1}H NMR spectrum of (a) pure **DPI** (20 mM), (b) probe **DPI** (20 mM) with the addition of hydrazine (1.0 equiv), and (c) Dansyl-NH_2 (20 mM)

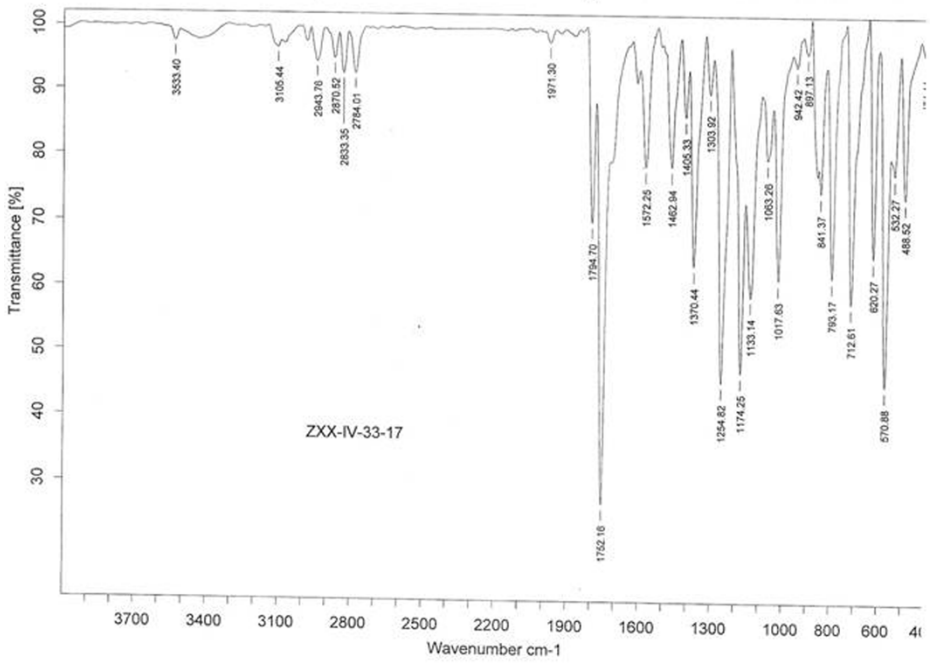

Figure S9. IR spectrum of **DPI**

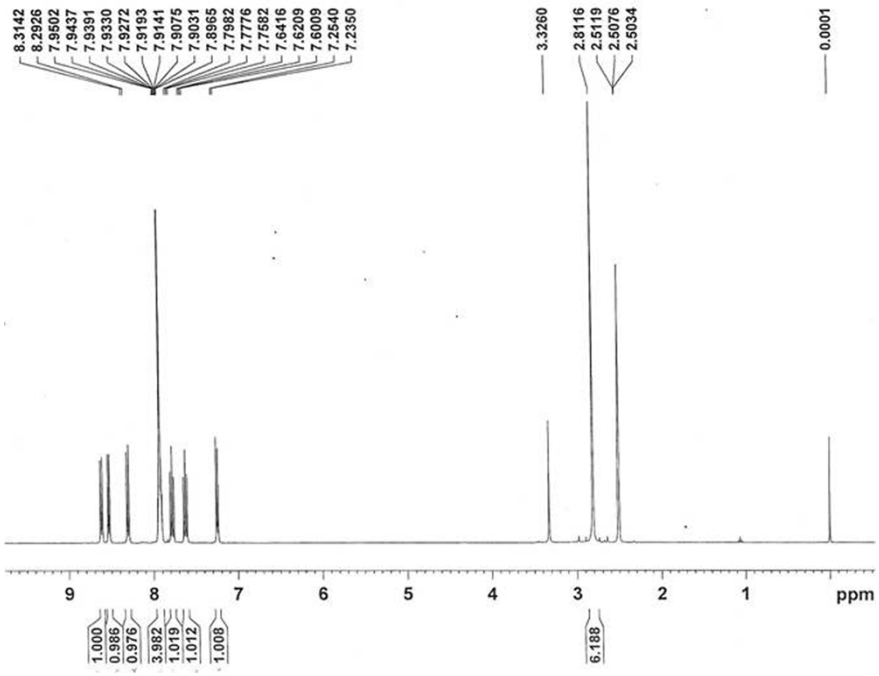

Figure S10. ^{1}H NMR spectrum of **DPI** in DMSO

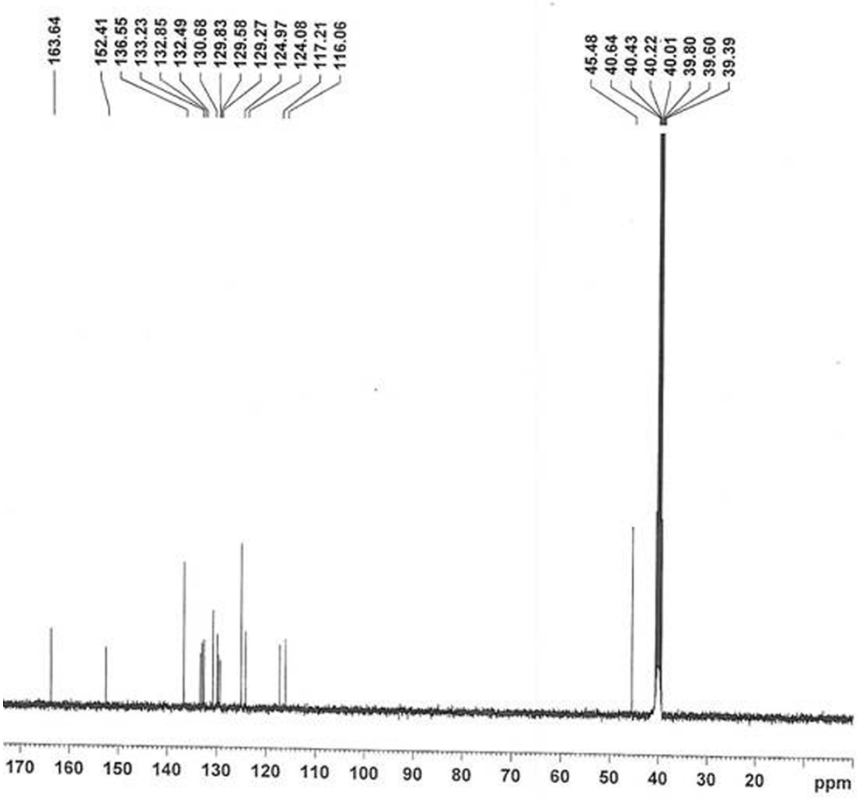

Figure S11. ^{13}C NMR spectrum of **DPI** in DMSO

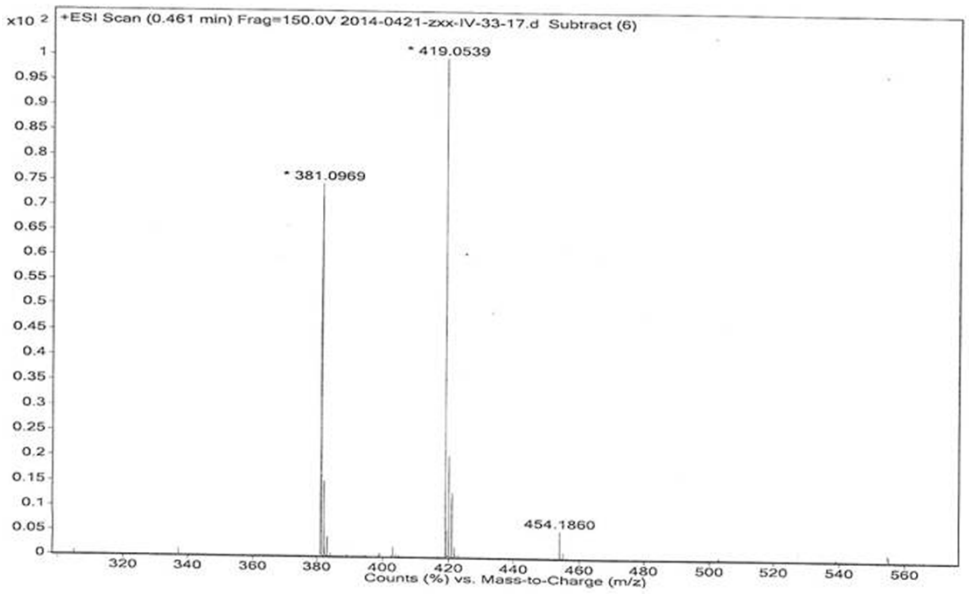

Figure S12. HRMS spectrum of **DPI**

7. References:

[1] C. A. Parker and W. T. Rees, *Analyst*, 1960, **85**, 587-600.

[2] B. Zhu, C. Gao, Y. Zhao, C. Liu, Y. Li, Q. Wei, Z. Ma, B. Du and X. Zhang, *Chem. Commun.*, 2011, **47**, 8656-8658.