

*Electronic Supplementary Information (ESI)*

**Highly sensitive detection of low-level water contents in  
organic solvents and cyanide in aqueous media using novel  
solvatochromic AIEE fluorophores**

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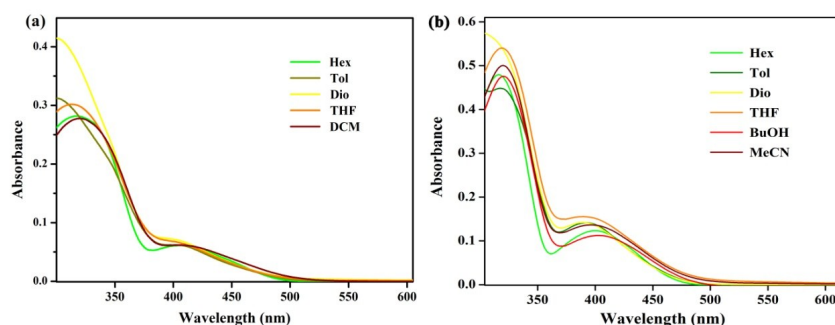
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# 1. Solvatochromism

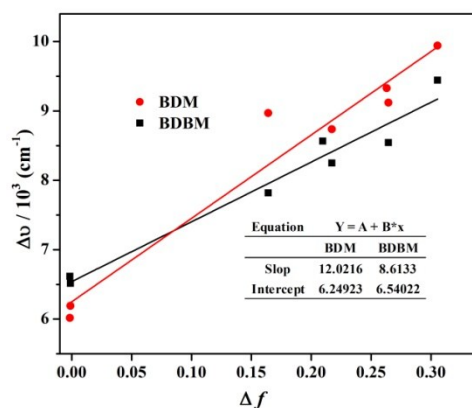
**Table 1** Photophysical properties of **BDM** and **BDBM** in various solvents.

Solvent <sup>a</sup>	$\Delta f^b$	$E_T^{N^c}$	BDM				BDBM			
			$\lambda_{abs}^d$ (nm)	$\lambda_{em}^e$ (nm)	$\Delta\nu^f$ (cm <sup>-1</sup> )	$\Phi_F^g$ (%)	$\lambda_{abs}^d$ (nm)	$\lambda_{em}^e$ (nm)	$\Delta\nu^f$ (cm <sup>-1</sup> )	$\Phi_F^g$ (%)
Cyc	-0.0016	0.006	407	539	6017	7	400	544	6618	6
Hex	-0.0011	0.009	403	537	6192	5	400	541	6516	9
Tol	0.0132	0.099	396	580	8011	10	392	561	7685	11
Dio	0.0223	0.164	387	597	9089	8	385	572	8492	11
Et <sub>2</sub> O	0.1641	0.117	393	607	8971	14	400	582	7818	10
THF	0.2096	0.207	389	615	9447	7	395	597	8566	6
DCM	0.2172	0.327	408	634	8737	3	404	606	8251	11
DMSO	0.2630	0.444	396	628	9329	<1	392	641	9510	1
BuOH	0.2644	0.586	394	615	9121	1	404	617	8545	2
MeCN	0.3055	0.460	390	637	9942	<1	395	630	9443	2

<sup>a</sup> Abbreviations: Hex, n-Hexane; Cyc, Cyclohexane; Tol, Toluene; Dio, Dioxane; Et<sub>2</sub>O, ethylether; THF, Tetrahydrofuran; DCM, Dichloromethane; DMSO, Dimethyl sulfoxide; BuOH, n-Butanol; MeCN, Acetonitrile. <sup>b</sup>  $\Delta f = (\epsilon - 1) / (2\epsilon + 1) - (n^2 - 1) / (2n^2 + 1)$  accounts for the spectral shifts due to reorientation of the solvent molecules, called the orientation polarizability, where  $\epsilon$  is solvent dielectric constant and  $n$  is index of refraction. <sup>c</sup>  $E_T^N$ , empirical parameters of solvent polarity. <sup>d</sup>  $\lambda_{abs}$ , absorption maximum wavelength. <sup>e</sup>  $\lambda_{em}$ , emission maximum wavelength. <sup>f</sup>  $\Delta\nu$ , Stokes shift. <sup>g</sup>  $\Phi_F$ , fluorescence quantum yield.

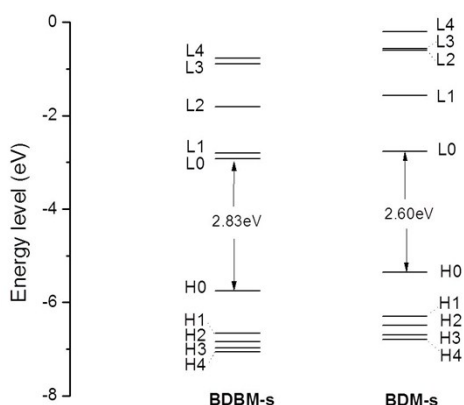


**Fig. S1** Absorption spectra of (a) **BDM** and (b) **BDBM** in different solvents. Concentration: 10  $\mu\text{mol}\cdot\text{L}^{-1}$ .



**Fig. S2** Plot of Stokes shift ( $\Delta f$ ) of **BDM** and **BDBM** versus  $\Delta\nu$  in different solvent.

## 2. Calculated vertical transition information and dipole moment



**Fig. S3** Energy levels of frontier molecular orbitals of **BDBM** and **BDM**.

**Table S2** Computed excitation energies, oscillator strengths and molecular orbital compositions of low-lying excited states of **BDBM** and **BDM**.

Compound	State	Excitation energy	Oscillator strength ( <i>f</i> )	MO composition
<b>BDBM</b>	S <sub>1</sub>	2.90 eV, 426 nm	0.1077	H-0 → L+0 (83%)
	S <sub>2</sub>	3.24 eV, 382 nm	0.5008	H-0 → L+1 (93%)
	S <sub>3</sub>	3.82 eV, 324 nm	0.3145	H-1 → L+1 (29%)
				H-2 → L+1 (25%)
				H-0 → L+2 (18%)
S <sub>4</sub>	3.92 eV, 316 nm	1.0619	H-5 → L+0 (11%)	
S <sub>5</sub>	4.04 eV, 306 nm	0.3180	H-2 → L+0 (33%)	
			H-1 → L+0 (54%)	
<b>BDM</b>	S <sub>1</sub>	2.93 eV, 423 nm	0.2107	H-0 → L+0 (86%)
	S <sub>2</sub>	3.73 eV, 332 nm	0.7414	H-0 → L+1 (79%)
	S <sub>3</sub>	3.75 eV, 330 nm	0.3755	H-1 → L+0 (55%)
				H-2 → L+0 (15%)
	S <sub>4</sub>	4.14 eV, 299 nm	0.0077	H-7 → L+0 (34%)
H-2 → L+0 (27%)				
H-1 → L+0 (10%)				
S <sub>5</sub>	4.33 eV, 286 nm	0.0845	H-3 → L+0 (20%)	
			H-7 → L+0 (19%)	
			H-1 → L+0 (17%)	
				H-5 → L+0 (12%)
				H-6 → L+0 (11%)

**Table S3** The dipole moments in the ground ( $\mu_g$ ) and the first excited ( $\mu_e$ ) states for **BDM** and **BDBM**.

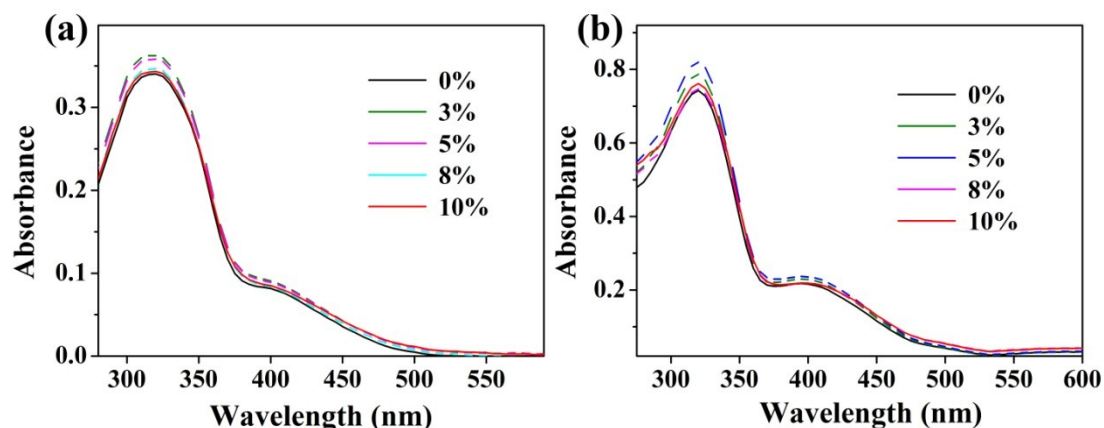
	$\mu_g$ /Debye e	$\mu_e$ /Debye	$ \mu_e - \mu_g $ /Debye e
<b>BDM</b>	9.7	22.9	13.2

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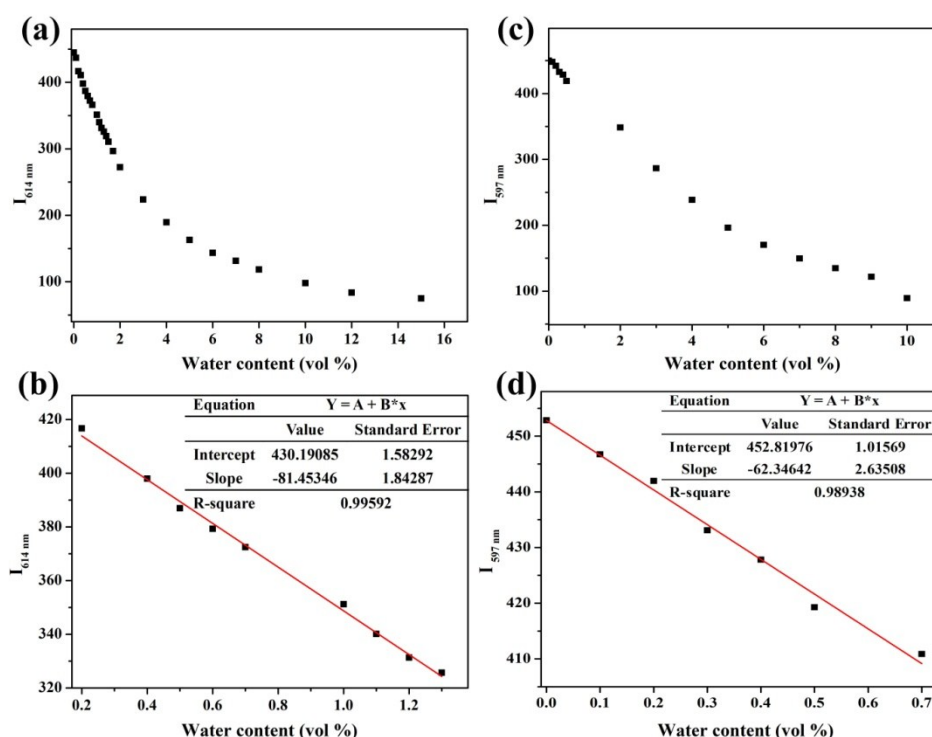
<b>BDBM</b>	19.6	30.1	10.5
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### 3. Detection of low-level water

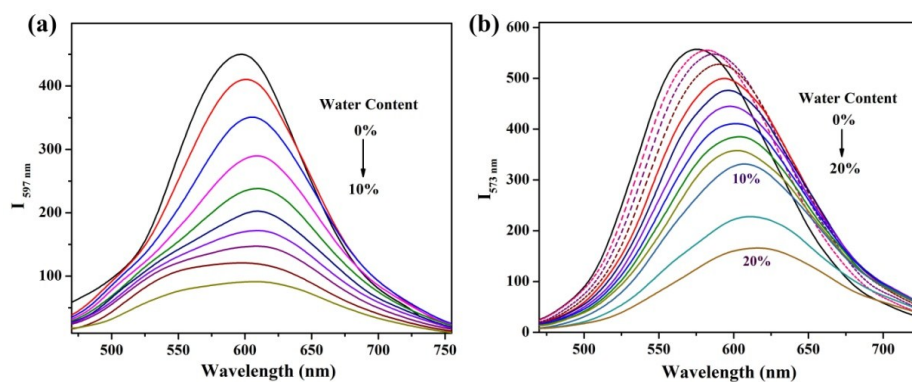


**Fig. S4** Absorption spectra of (a) **BDM** and (b) **BDBM** in THF solution in the presence of increasing amount of water.



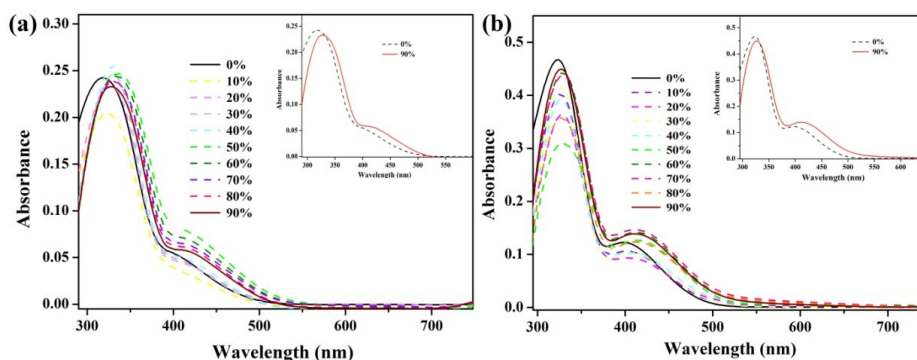
**Fig. S5** (a) Fluorescent peak intensity of **BDM** at 614 nm in THF (a) and at 597 nm in dioxane (c) with increasing water content. (b) Plot of fluorescent intensity change of **BDM** versus varied concentrations of H<sub>2</sub>O in THF solution.  $\lambda_{ex} = 400$  nm,  $\lambda_{em} = 614$  nm,  $R^2 = 0.99592$ ,  $k = -8145.3$ ,  $\sigma = 0.28$ . The Standard deviation ( $\sigma$ ) was obtained by fluorescence responses (10-times of consecutive scanning on the Varian Cary Eclipse Fluorescence Spectrophotometer). The detection limit was calculated by the formula ( $3\sigma/|k|$ ) giving the result of 0.010%. (d) Plot of fluorescent intensity change of **BDM**

versus varied concentrations of H<sub>2</sub>O in dioxane solution.  $\lambda_{\text{ex}} = 400 \text{ nm}$ ,  $\lambda_{\text{em}} = 597 \text{ nm}$ ,  $R^2 = 0.98938$ ,  $k = -6234.6$ ,  $\sigma = 0.39$ . The Standard deviation ( $\sigma$ ) was obtained as aforementioned and the detection limit was calculated as 0.019%.



**Fig. S6** Fluorescence spectra of (a) **BDM** and (b) **BDBM** in dioxane solution in the presence of increasing amount of water.

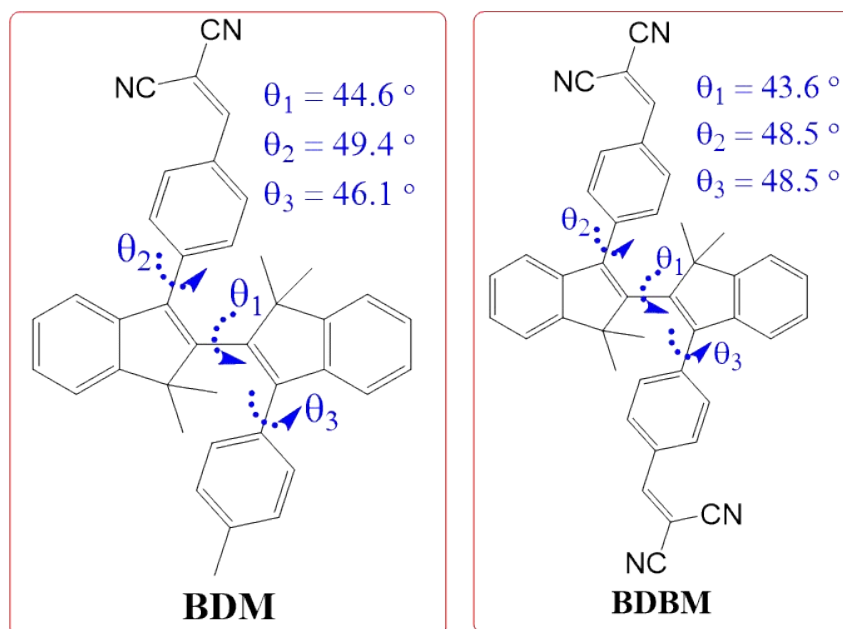
#### 4. AIEE behaviours and optimized geometries



**Fig. S7** Absorption spectra of **BDM** (a) and **BDBM** (b) in DMSO/water mixtures with different water contents. Concentration: 10  $\mu\text{M}$ .

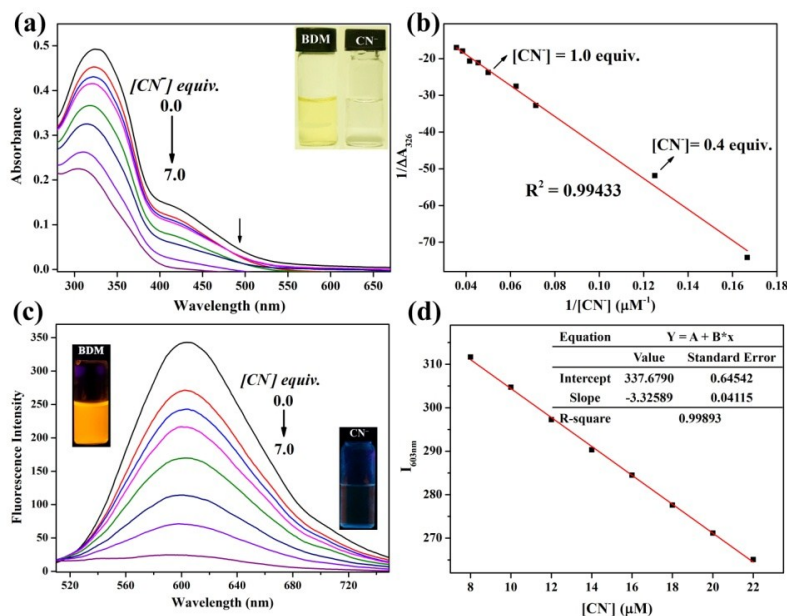
**Table S4** Computed free energies of the compounds.

	Self-consistent field energy	Zero-point energy	Thermal correction	Relative free energy
<b>BDBM-s</b>	-1837.60442530 a.u.	0.600123 a.u.	0.529692 a.u.	
<b>BDBM-t</b>	-1837.59839243 a.u.	0.600331 a.u.	0.526311 a.u.	7.5 kJ/mol, w.r.t. <b>BDBM-s</b>
<b>BDM-s</b>	-1615.04011757 a.u.	0.596619 a.u.	0.531220 a.u.	
<b>BDM-t</b>	-1615.03486889 a.u.	0.596881 a.u.	0.528109 a.u.	6.3 kJ/mol, w.r.t. <b>BDM-s</b>

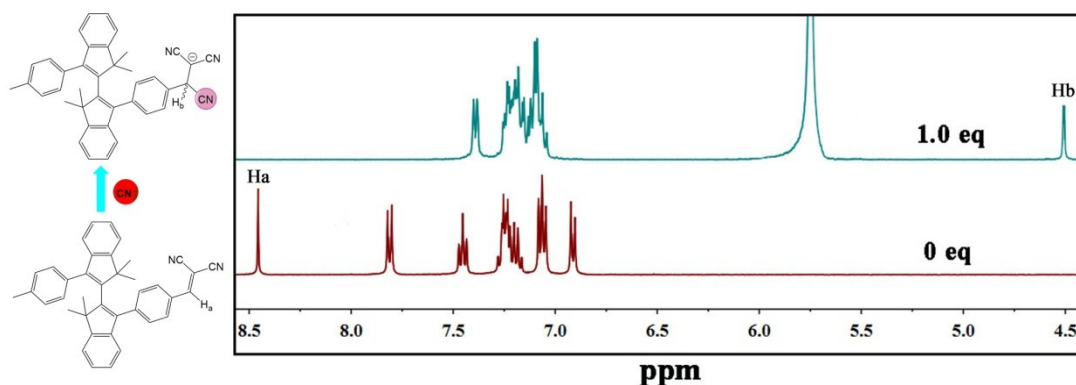


**Fig. S8** Calculated dihedral angles of compound **BDBM** and **BDM**.

## 5. Detection of cyanide and supporting calculation

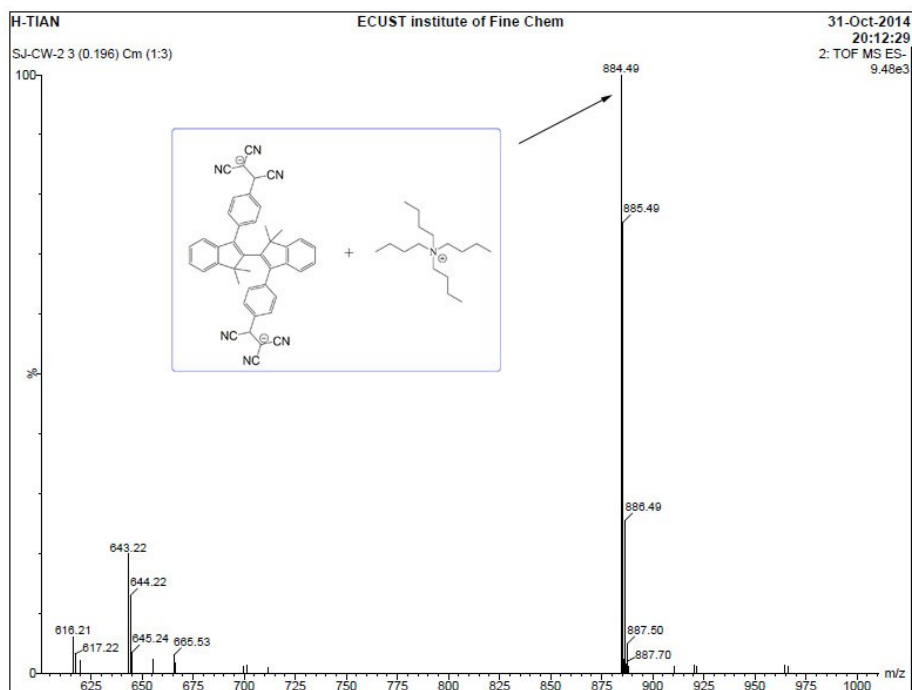


**Fig. S9** (a) Absorption spectral changes of **BDM** (20  $\mu\text{M}$ ) upon the addition of 0-7.0 equiv. cyanide in 2 mM CTAB micellar solution. Insert: the images of **BDM** with different amount of cyanide (left: none; right: 7.0 equiv. cyanide). (b) Benesi–Hildebrand plot of absorbance at 326 nm. (c) Fluorescence spectra of **BDM** (20  $\mu\text{M}$ ) upon addition of 0-7.0 equiv. cyanide in 2 mM CTAB micellar solution. Insert: the images of fluorescence with different amounts of cyanide (left: none; right: 7.0 equiv. cyanide). (d) Plot of fluorescence intensity versus cyanide concentration,  $\lambda_{\text{ex}} = 400 \text{ nm}$ ,  $\lambda_{\text{em}} = 603 \text{ nm}$ ,  $R^2 = 0.99893$ ,  $k = -3.33 \mu\text{M}^{-1}$ ,  $\sigma = 0.36$ . The standard deviation ( $\sigma$ ) was obtained by fluorescence responses (10-times of consecutive scanning on the Varian Cary Eclipse Fluorescence Spectrophotometer). The detection limit was calculated as  $0.32 \mu\text{M}$  by the formula  $(3\sigma/|k|)$ .

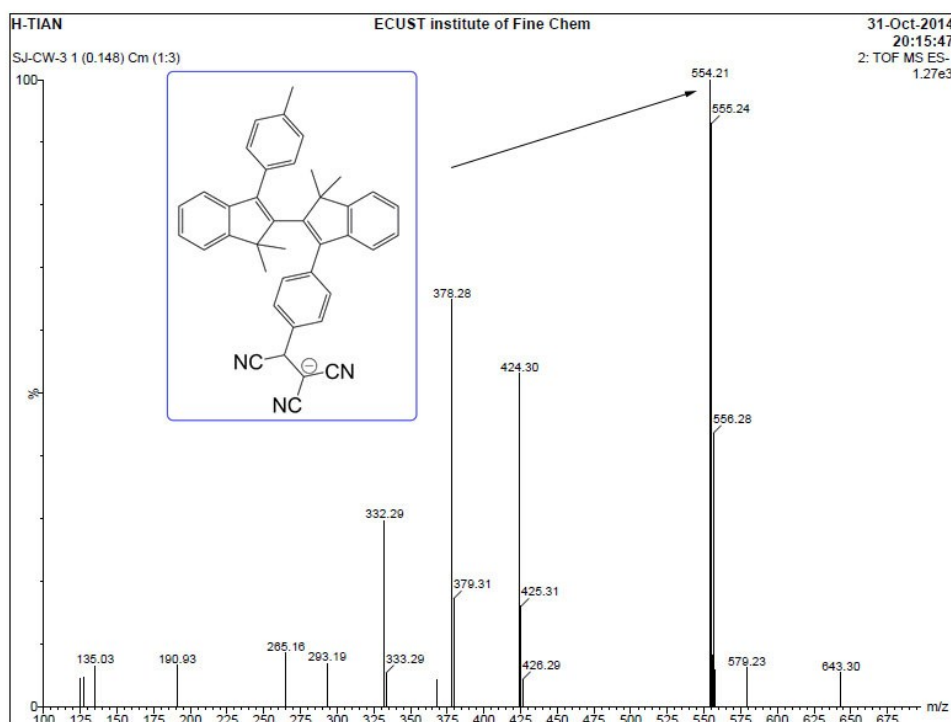


**Fig. S10**  $^1\text{H}$  NMR spectra of **BDM** in  $\text{DMSO-}d_6$  upon addition of cyanide anion in  $\text{CH}_2\text{Cl}_2$ .

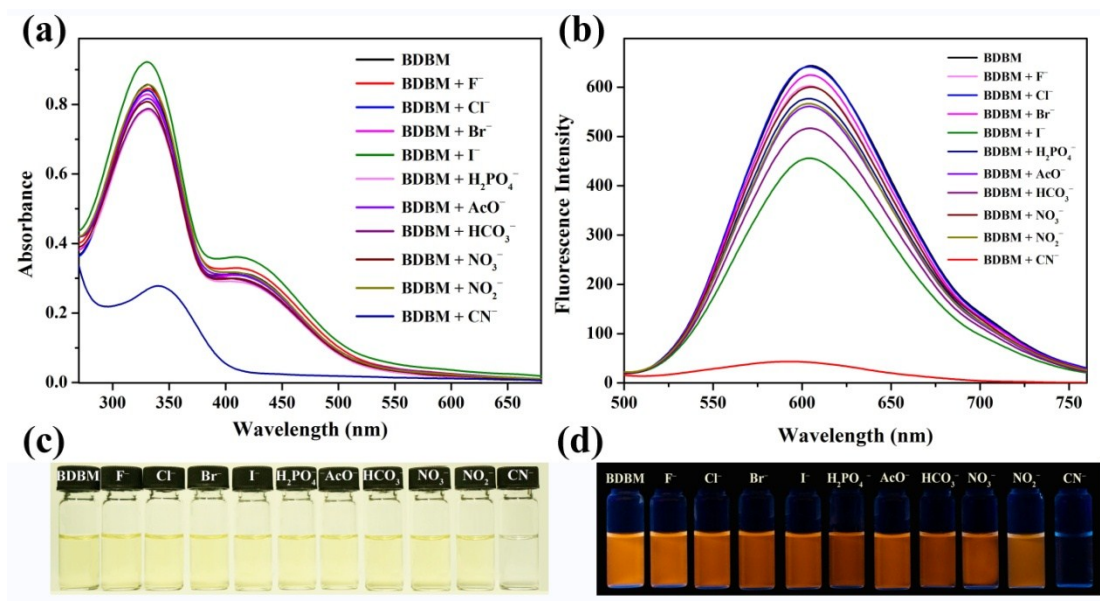




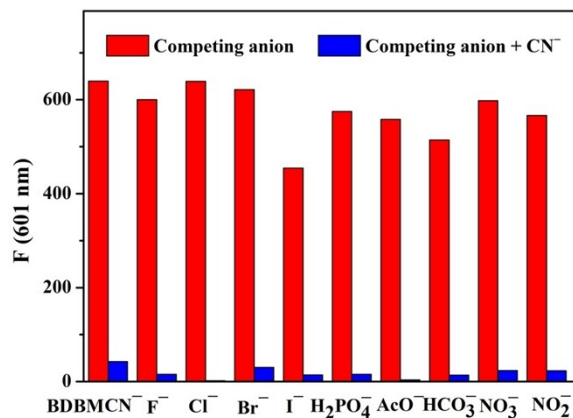
**Fig. S11** MS (ESI-) spectrum of compound **BDBM** (10  $\mu$ M) with  $\text{CN}^-$  (25  $\mu$ M) in  $\text{CH}_2\text{Cl}_2$  solution at 25  $^\circ\text{C}$ . Calcd for  $\text{C}_{60}\text{H}_{66}\text{N}_7^- = 884.54$ , found: 884.49.



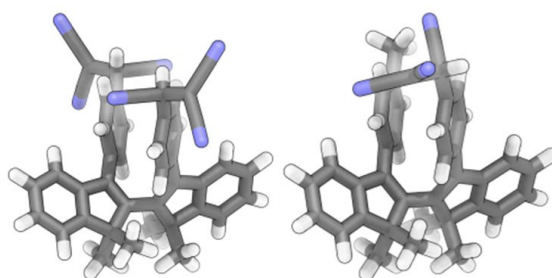
**Fig. S12** MS (ESI-) spectrum of compound **BDM** (10  $\mu$ M) with  $\text{CN}^-$  (15  $\mu$ M) in  $\text{CH}_2\text{Cl}_2$  solution at 25  $^\circ\text{C}$ . Calcd for  $\text{C}_{40}\text{H}_{32}\text{N}_3^- = 554.26$ , found: 554.21.



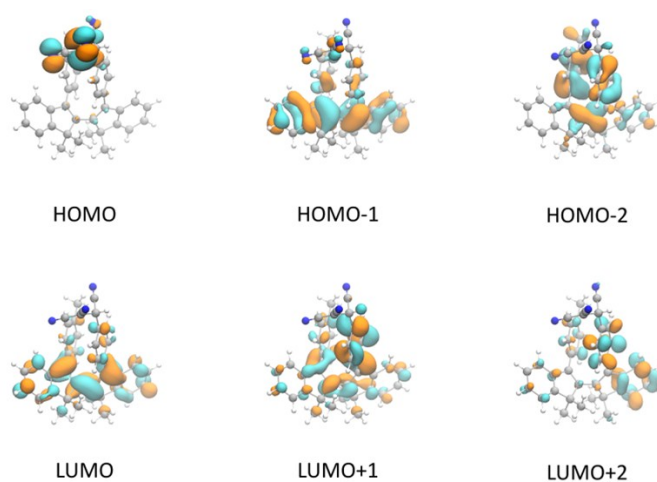
**Fig. S13** (a) Absorption spectra and (b) fluorescence of **BDBM** in CTAB micelles (2 mM) upon addition of various anions (CN<sup>-</sup>: 9.0 equiv., other anions: 45.0 equiv.). The corresponding colour (c) and emission (d) changes of **BDBM** in CTAB micelles (2 mM) upon addition of various anions. Concentration: 20 μM; excitation wavelength: 400 nm.



**Fig. S14** The fluorescence intensity changes at 601 nm of **BDBM** (20 mM) upon addition of 9.0 equiv. of CN<sup>-</sup> and 45.0 equiv. of various interference anions.



**Fig. S15** Optimized geometries of (left) [CN-BDBM-CN]<sup>2-</sup> and (right) [CN-BDM]<sup>-</sup>.



**Fig. S16** Frontier molecular orbitals of  $[\text{CN-BDM}]^-$ .

**Table S5** Computed excitation energies, oscillator strengths and molecular orbital compositions of low-lying excited states of  $[\text{CN-BDBM-CN}]^{2-}$  and  $[\text{CN-BDM}]^-$ .

Compound	State	Excitation energy	Oscillator strength ( $f$ )	MO composition
$[\text{CN-BDBM-CN}]^{2-}$	$S_1$	3.56 eV, 348 nm	0.4597	H-2 $\rightarrow$ L+0 (73%) H-0 $\rightarrow$ L+0 (21%)
	$S_2$	3.94 eV, 314 nm	0.0201	H-0 $\rightarrow$ L+1 (13%)
	$S_3$	3.94 eV, 314 nm	0.0259	H-1 $\rightarrow$ L+1 (13%)
	$S_4$	4.42 eV, 280 nm	0.1482	H-1 $\rightarrow$ L+0 (29%) H-0 $\rightarrow$ L+1 (22%) H-2 $\rightarrow$ L+1 (13%)
	$S_5$	4.46 eV, 277 nm	0.0042	H-2 $\rightarrow$ L+1 (50%) H-1 $\rightarrow$ L+0 (24%)
$[\text{CN-BDM}]^-$	$S_1$	3.47 eV, 356 nm	0.3927	H-1 $\rightarrow$ L+0 (87%)
	$S_2$	4.11 eV, 301 nm	0.0025	H-0 $\rightarrow$ L+16 (41%)
	$S_3$	4.31 eV, 287 nm	0.0291	H-0 $\rightarrow$ L+0 (63%) H-0 $\rightarrow$ L+1 (10%)
	$S_4$	4.57 eV, 271 nm	0.0194	H-2 $\rightarrow$ L+0 (38%) H-1 $\rightarrow$ L+1 (35%)
	$S_5$	4.63 eV, 267 nm	0.1764	H-2 $\rightarrow$ L+0 (42%) H-1 $\rightarrow$ L+1 (32%)

## 6. $^1\text{H}$ , $^{13}\text{C}$ NMR, HRMS and Crystal data for sensors and products

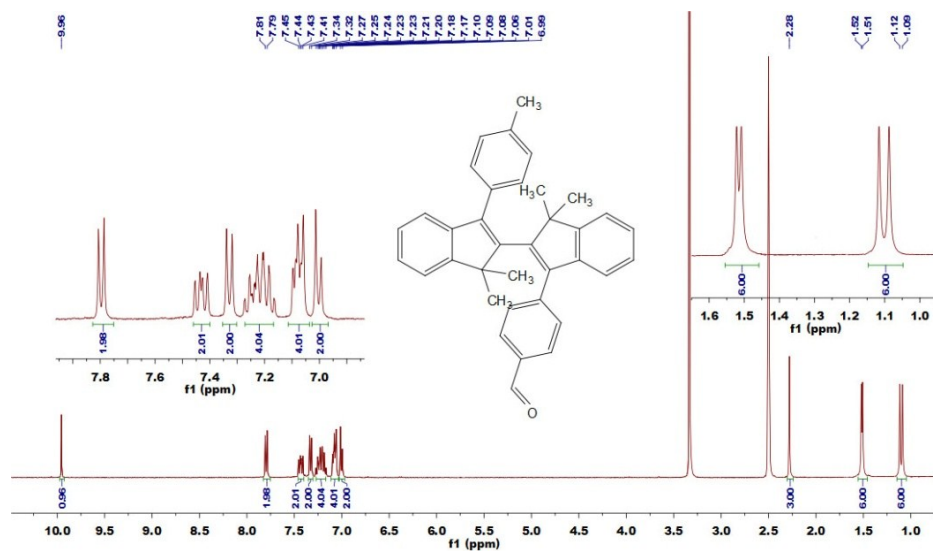


Fig. S17  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of compound 2.

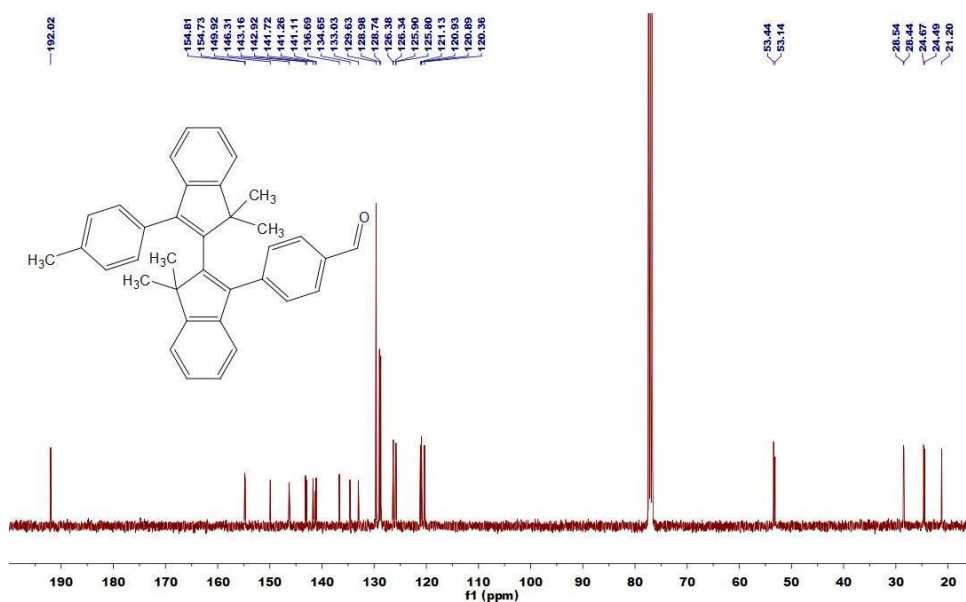


Fig. S18  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound 2.

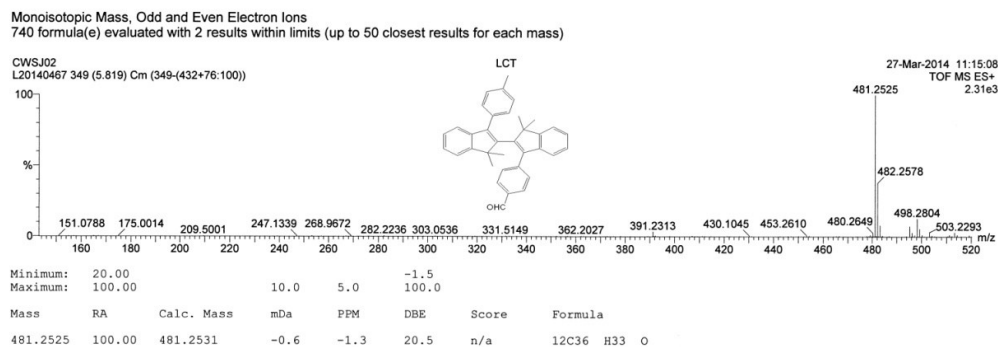


Fig. S19 ESI-MS spectrum of compound 2.

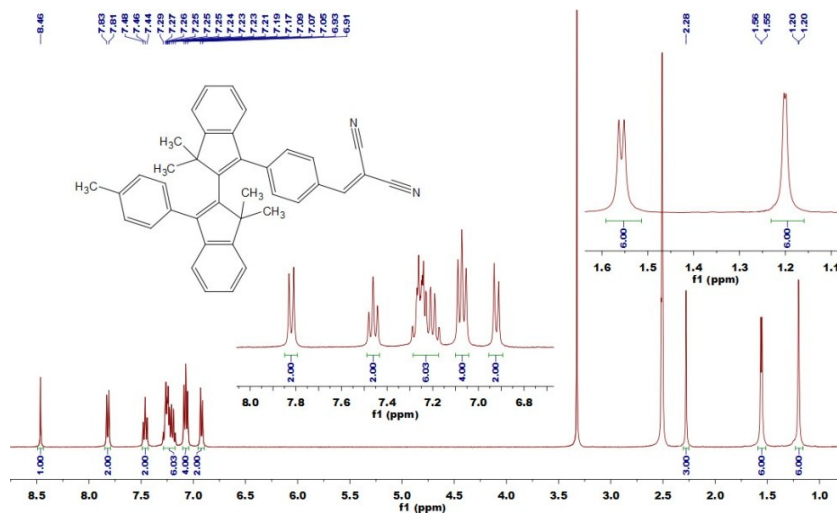


Fig. S20  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **BDM**.

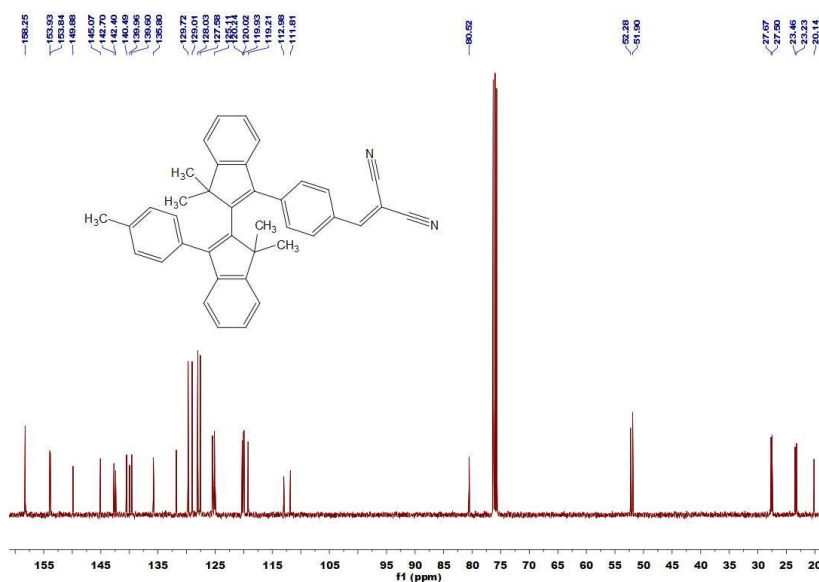


Fig. S21  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **BDM**.

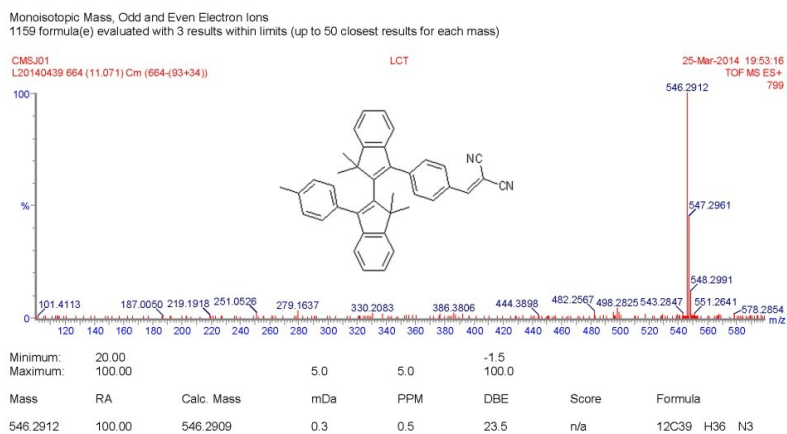


Fig. S22 ESI-MS spectrum of compound **BDM**.

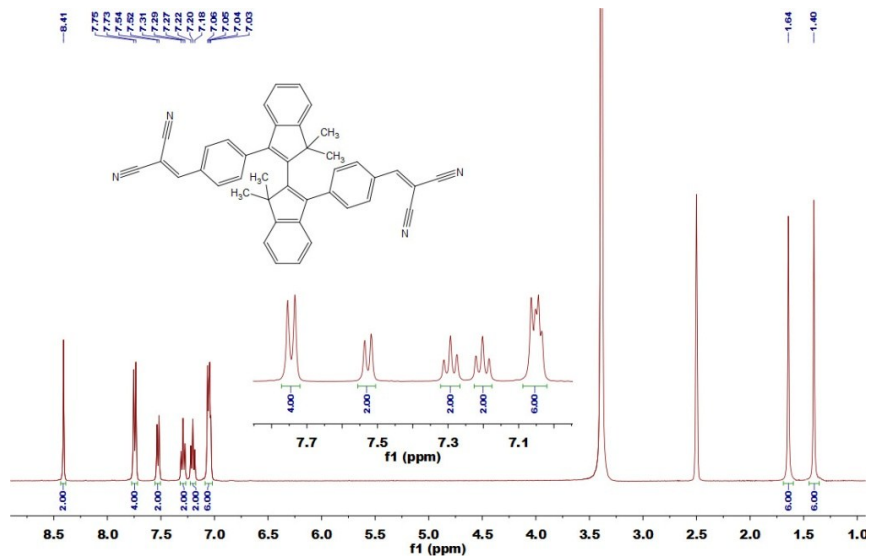


Fig. S23  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **2**.

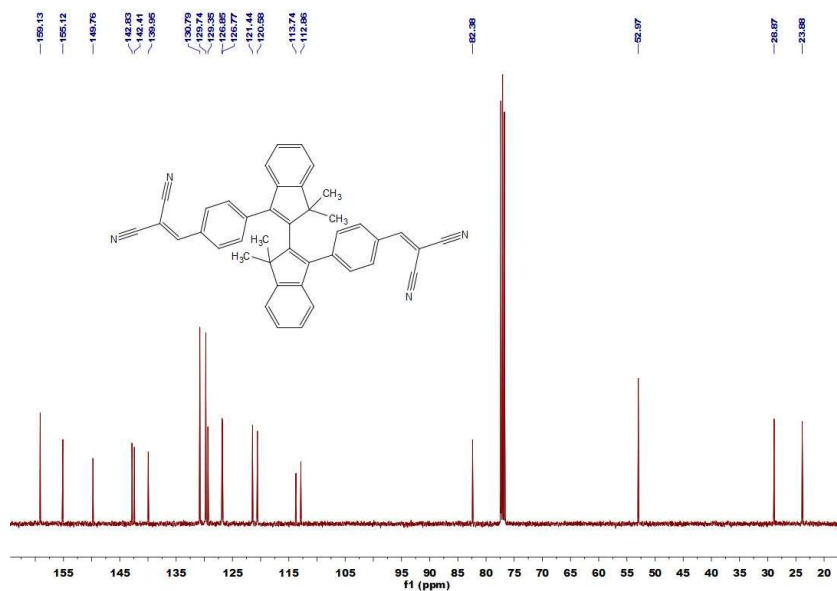
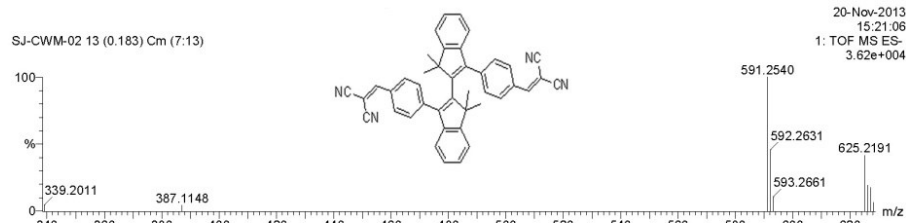


Fig. S24  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **BDBM**.

Monoisotopic Mass, Odd and Even Electron Ions  
 18 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)  
 Elements Used:  
 C: 0-50 H: 0-40 N: 0-4

SJ-CWM-02 13 (0.183) Cm (7:13)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
591.2540	591.2549	-0.9	-1.5	29.5	18.3	0.0	$\text{C}_{42}\text{H}_{31}\text{N}_4$

Fig. S25 ESI-MS spectrum of compound **BDBM**.

**Table S6** Crystal data and structure refinement for compound **BDBM**.

<b>BDBM</b>	
Empirical formula	C <sub>42</sub> H <sub>30</sub> N <sub>4</sub>
Formula weight	590.7
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
a	17.624(4) Å
b	13.658(3) Å
c	14.035(3) Å
$\alpha$	90°
$\beta$	108.504(4)°
$\gamma$	90°
Volume	3203.8(11) Å <sup>3</sup>
Z	4
Density (calculated)	1.225 Mg/m <sup>3</sup>
Absorption coefficient	0.072 mm <sup>-1</sup>
F(000)	1240
Crystal size	0.211 x 0.175 x 0.123 mm <sup>3</sup>
Theta range for data collection	1.926 to 25.999°.
Index ranges	-21<=h<=21, -16<=k<=16, -14<=l<=17
Reflections collected	9452
Independent reflections	3154 [R(int) = 0.0593]
Completeness to theta = 25.242°	99.90%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6353
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3154 / 0 / 211
Goodness-of-fit on F <sup>2</sup>	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0643, wR <sub>2</sub> = 0.1528
R indices (all data)	R1 = 0.0799, wR <sup>2</sup> = 0.1670
Extinction coefficient	0.0095(12)
Largest diff. peak and hole	0.343 and -0.285 e.Å <sup>-3</sup>
CCDC number	1016979

## 7. Full Listing for Reference 74

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Lyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochtersk, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, revision A.2; Gaussian, Inc.: Wallingford CT, 2009.