Supporting Information

3D Cross-Correlative Matrix Temperature Detection and Non-Invasive Thermal Mapping based on a Molecular Probe

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Section A. Materials and method

All chemicals and reagents were purchased from Alfa Aesar and Beijing Chemical Reagent Company without further purification. Solvents were purified according to standard procedures. ^{1}H NMR spectra were recorded on a Bruker ARX-400. MALDI-TOF-MS spectra were measured by a Bruker BIFLEX III spectrometer. UV-vis absorption spectra were recorded on a TU-1901 spectrophotometer. Photoluminescence spectra were carried out on a F-4500 spectrophotometer. Powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. The theoretical ground-state geometry and electronic structure of MCBD were optimized using the density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31+G**.All the theoretical calculations were performed using Gaussian 03 package.[1] IR spectra were performed on an IRPrestige-21 spectrometer usingKBr pellets in the frequency range of 4000-500 cm^{-1}.Accurate temperature was calibrated by using GP-100 thermometer with Model 12C temperature monitor 2(Cryogenic Control Systems, Inc).

Lippert-Mataga equation:

$$\Delta\upsilon \equiv \upsilon_{ab}-\upsilon_{em} = \frac{2\Delta f}{hca^3}(\mu_e-\mu_g)^2 + \text{constant}$$

$$\Delta f = f(\varepsilon) - f(n^2) \approx \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}$$

$\Delta\upsilon$ is the Stokes shift, h is the Planck constant, c is the speed of light, a is the Onsager cavity radius, μ_e and μ_g refer to the dipolar moments in the excited and ground states, and ε and n are the dielectric constant and refractive index of the solvent, respectively.

Permittivity and refractivity of a solvent are known to decrease with an increase in temperature (T) in a nonlinear fashion, as expressed by the following empirical equations:

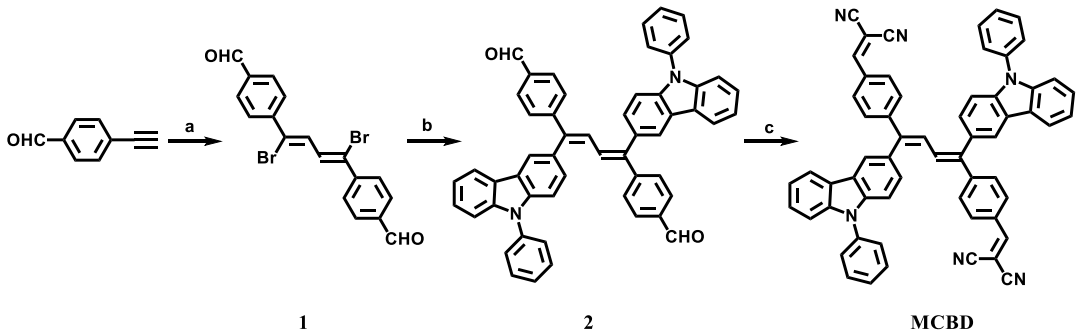
$$\varepsilon = \varepsilon_0-\alpha(T - T_0) - \beta(T - T_0)^2- \gamma(T - T_0)^3$$

$$n = n_0- a(T - T_0) - b(T - T_0)^2$$

Combined with the Lippert-Mataga equation, the above equations indicate that the polarity of a solvent should decrease along with the temperature rising.

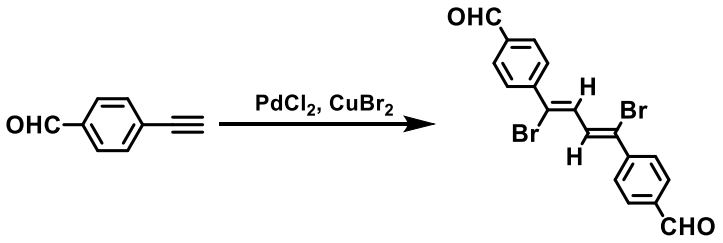
The relative sensitivity of each probe was calculated according to the equation $S_{rel}(T) = |\partial I/\partial T|/I$, where I is the intensity (the measured temperature-sensitive parameter). The internal sensitivity was calculated according to the equation $S_{int}(T) = |\partial(I_1/(I_1+I_2))/\partial T|$.

Section B. Synthetic procedures

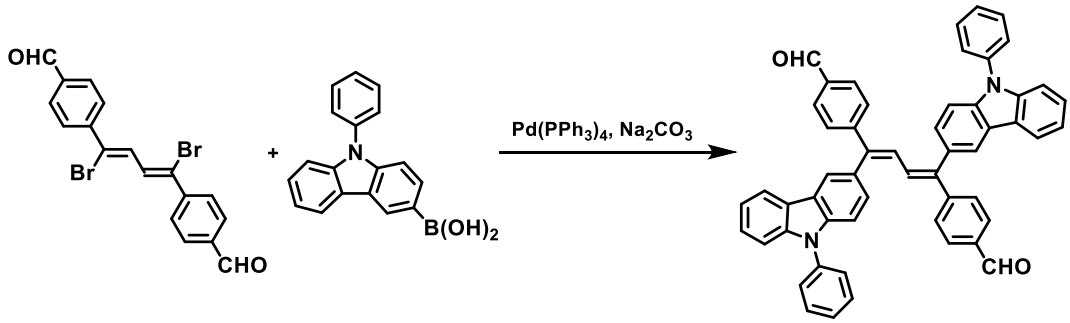


1 2 MCBD

Synthetic route to MCBD. Synthesis and structure of the molecular probe described in this paper. a: $PdCl_2$, $CuBr_2$, r.t.; b: 9-Phenyl-9H-carbazol-3-ylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, reflux; c: malonitrile, Et_3N, r.t..

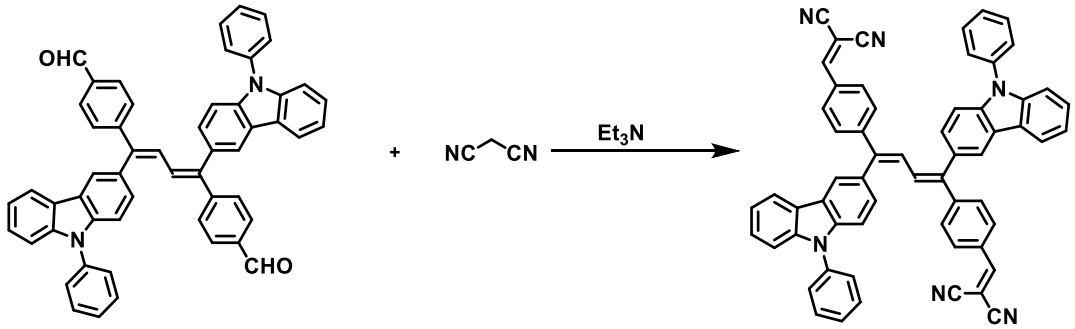


Preparation of 1.A mixture of benzaldehyde (20 mmol), $PdCl_2$ (1 mmol) and $CuBr_2$ (60 mmol) in acetonitrile/toluene (2/100 mL) was stirred for 24 h at room temperature. The crude product was purified by column chromatography (petroleum ether/dichloromethane), yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.90 (q, *J* = 8.4 Hz, 4H), 7.51 (s, 1H).EI-MS: m/z calcd. 420.1 for $C_{18}H_{12}Br_2O_2$, found 420.



Preparation of 2.A mixture of 1 (2.8 mmol), 9-Phenyl-9H-carbazol-3-ylboronic acid (8.5 mmol), $Pd(PPh_3)_4$ (0.28 mmol) and Na_2CO_3 (17 mmol) in toluene/methanol (3/1 in vol) was stirred under N_2 for 12 h at 70 ºC. The crude product was also purified by column chromatography (petroleum ether/dichloromethane),yield: 75%.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.15–8.08 (m, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 3.9 Hz, 4H), 7.47 (dd,

J = 15.0, 7.0 Hz, 4H), 7.42–7.37 (m, 3H), 7.30 (s, 1H), 7.08 (s, 1H).MALDI-TOF MS: m/z calcd. 744.2 for $C_{54}H_3N_2O_2$, found 744.5.



Preparation of MCBD.A mixture of 2 (0.2 mmol), malononitrile (1 mmol) and 2 drops of triethylamine in ethyl acetate (30 mL) was stirred at 50ºC for 4 h. The crude product was purified by column chromatography (petroleum ether/dichloromethane), yield: 33%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.15–8.08 (m, 2H), 7.71 (d, *J*= 8.3 Hz, 2H), 7.65 (d, *J*= 3.9 Hz, 4H), 7.52–7.43 (m, 4H), 7.39 (dd, *J* = 4.9, 3.3 Hz, 3H), 7.33–7.27 (m, 1H), 7.08 (s, 1H). MALDI-TOF MS: m/z calcd. 840.9 for $C_{60}H_{36}O_6$, found 840.6.

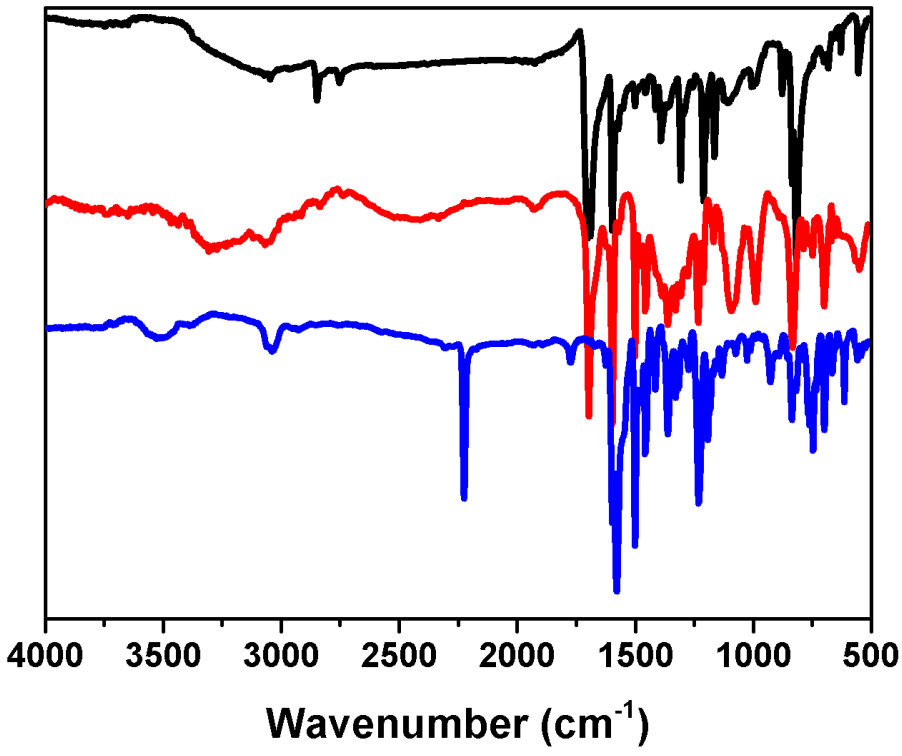


Figure S1. FT-IR spectra of 1 (black), 2 (red),and MCBD (blue).

Section C. Supplementary spectra (Figure S2-S10)

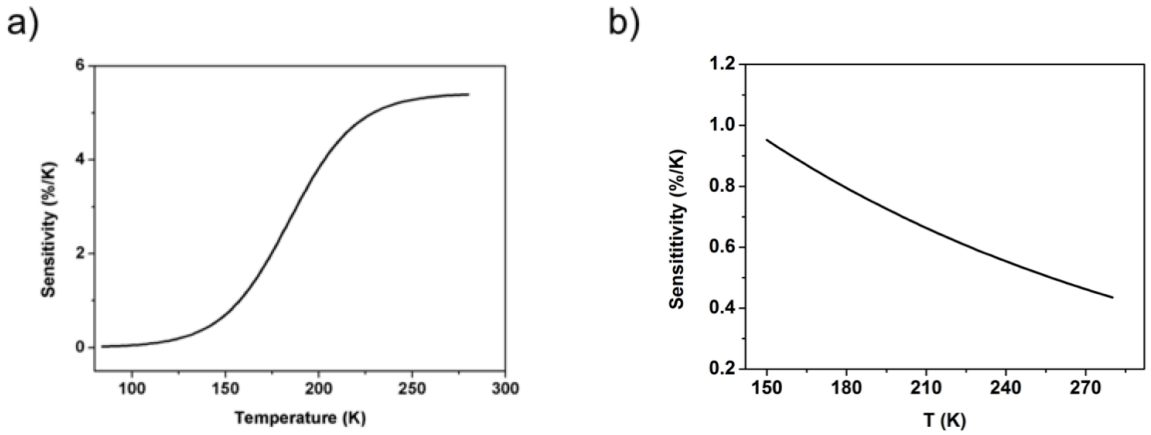


Figure S2. (a) Relative sensitivity and (b) internal sensitivity of MCBD in hexane. The relative sensitivity was calculated according to the equation $S_{rel}(T) = |\partial I_{560}/\partial T|/I_{560}$. The internal sensitivity was calculated according to the equation $S_{int}(T) = |\partial(I_{560}/(I_{560}+I_{640}))/\partial T|$.

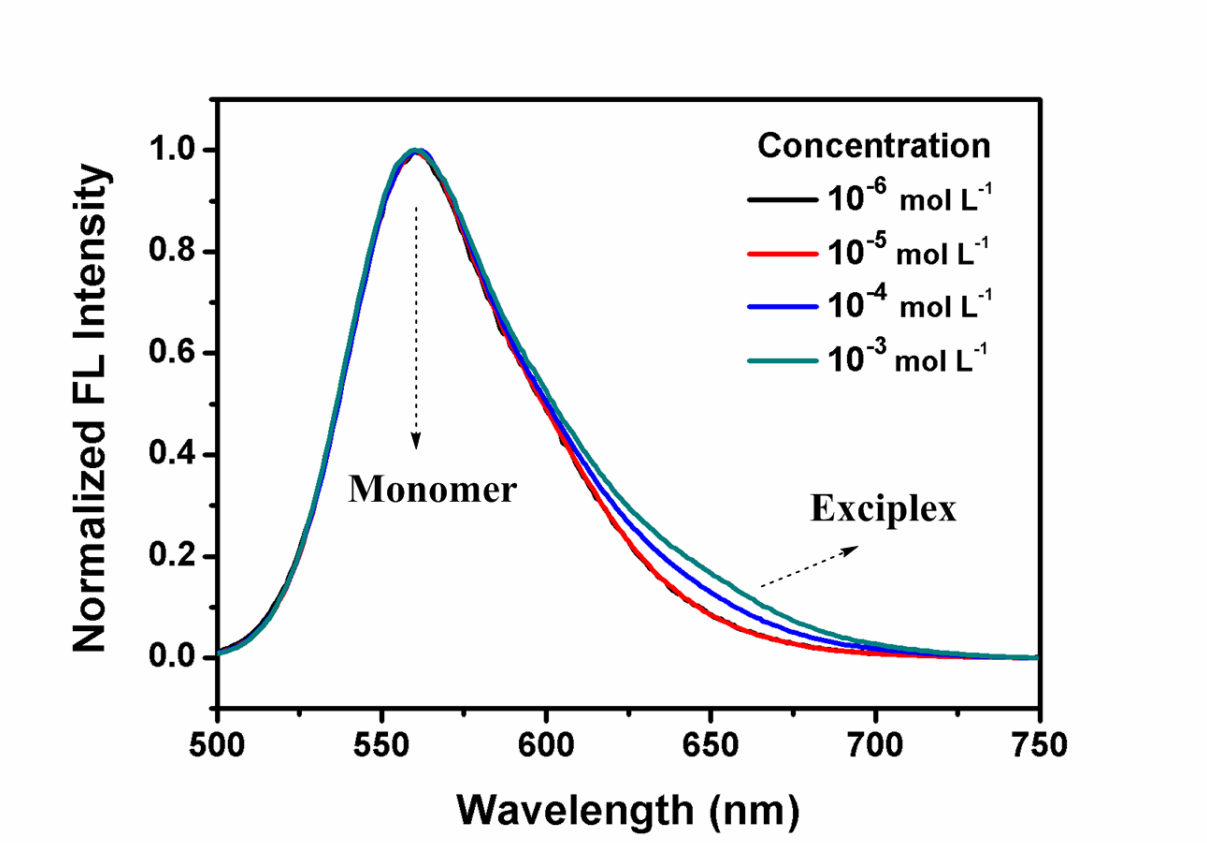


Figure S3. Emission spectra of MCBD in *n*-hexane with various concentrations. Excitation wavelength: 480 nm.

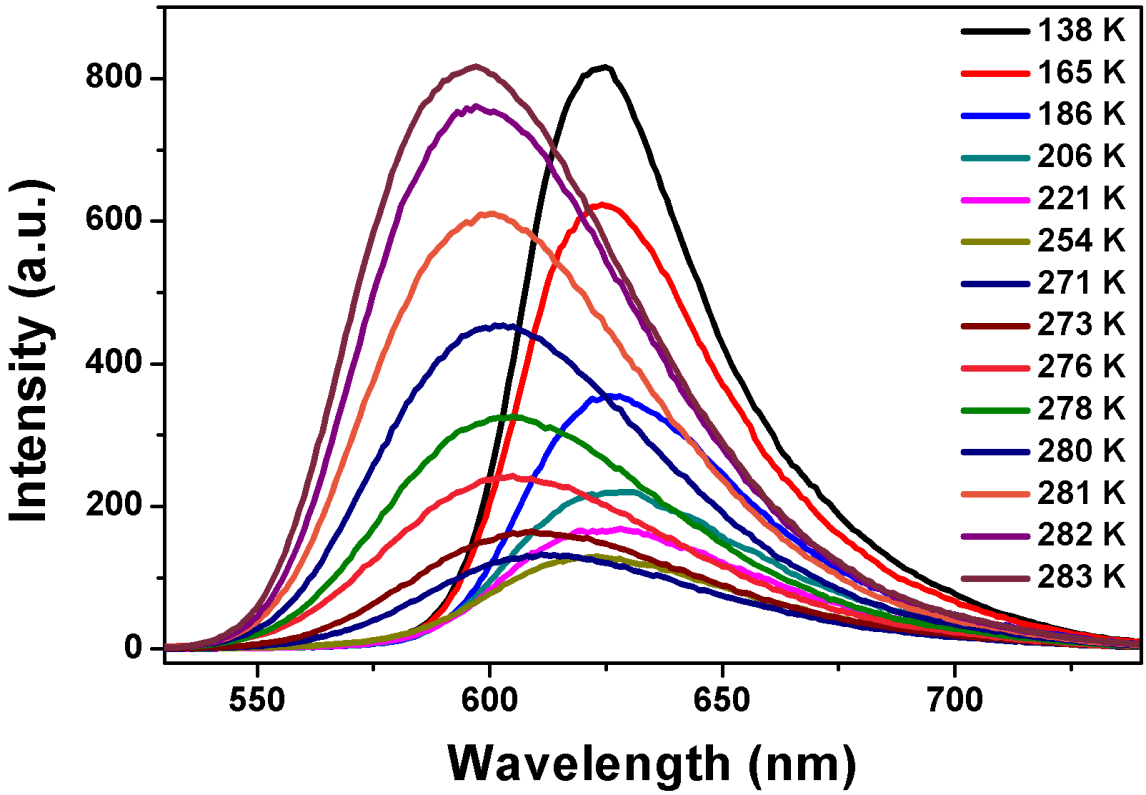


Figure S4. Temperature-dependent spectra of MCBD in dioxane. Excitation wavelength: 480 nm. Concentration: 2×10^{-4} M.

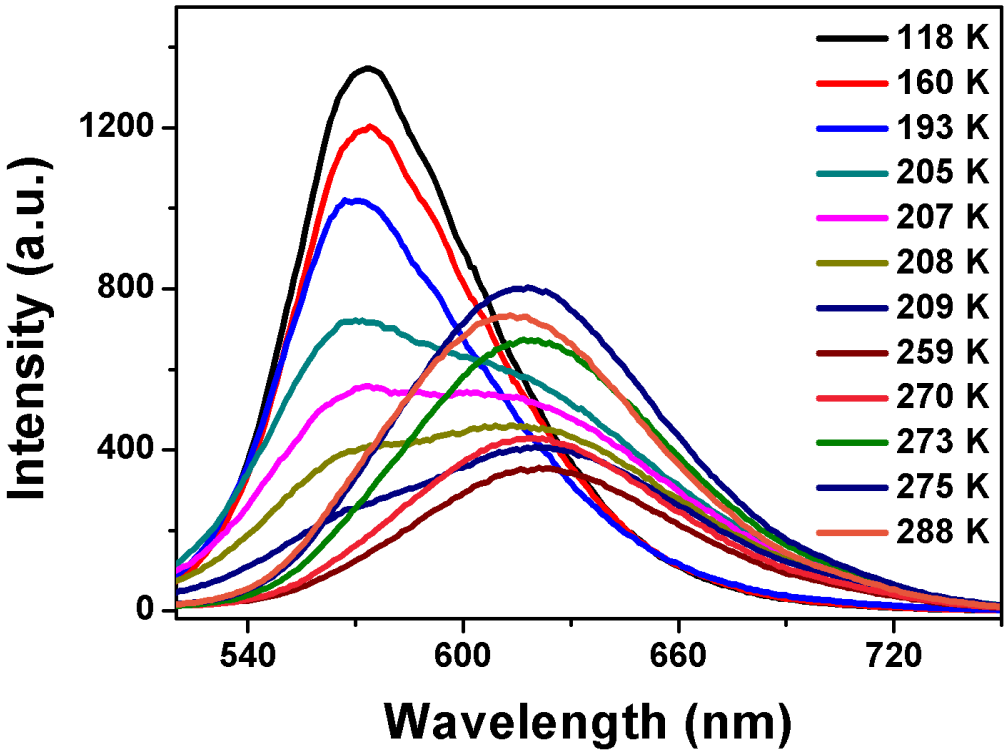


Figure S5. Emission spectra of MCBD in 1,2-dimethoxyethane. Excitation wavelength: 480 nm. Concentration: 10^{-5} M.

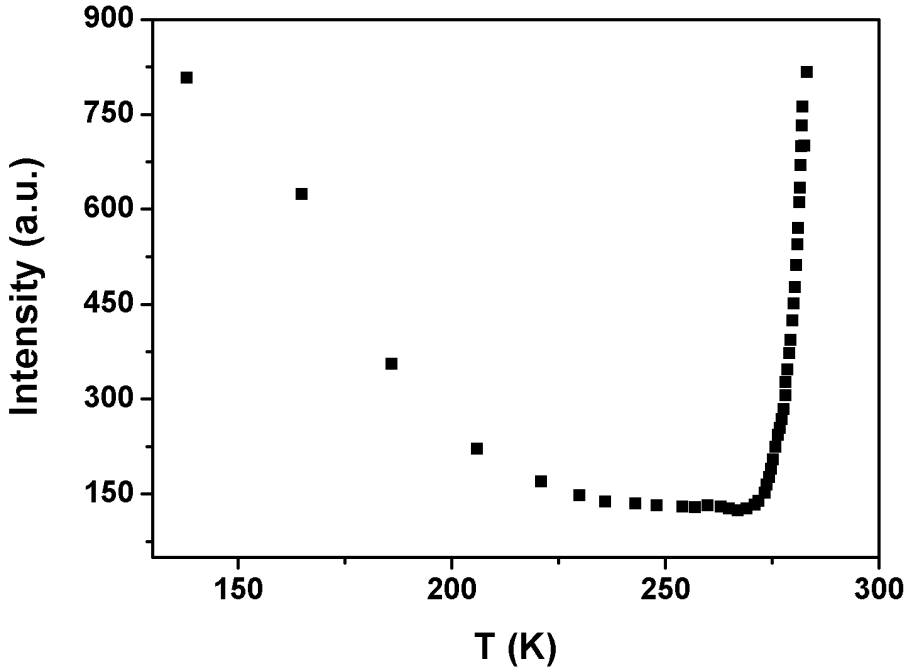


Figure S6. Temperature-dependence of the fluorescence intensity (I_{max}) of MCBD in dioxane.

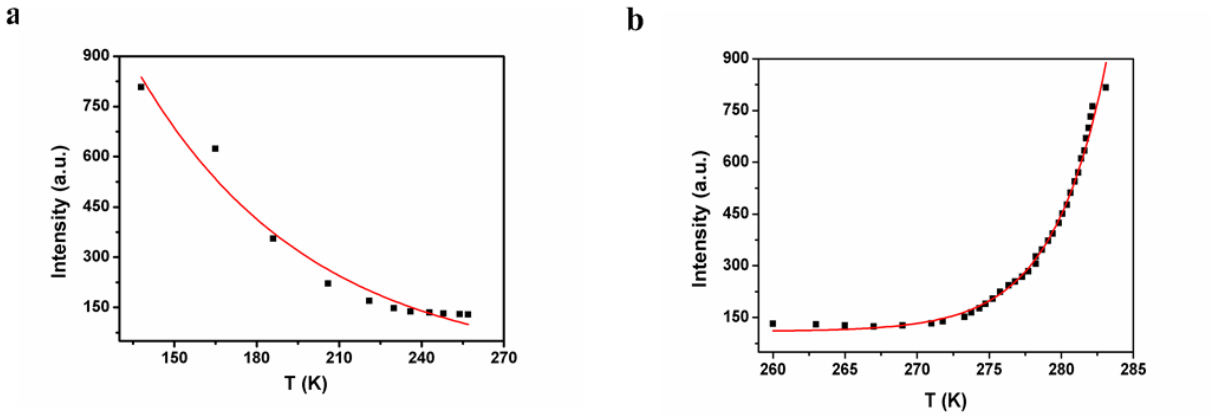


Figure S7. Temperature-dependence of the fluorescence intensity (I_{max}) of MCBD in dioxane in the temperature range (a) from 138 to 250 K, and(b) from 260 to 283 K.

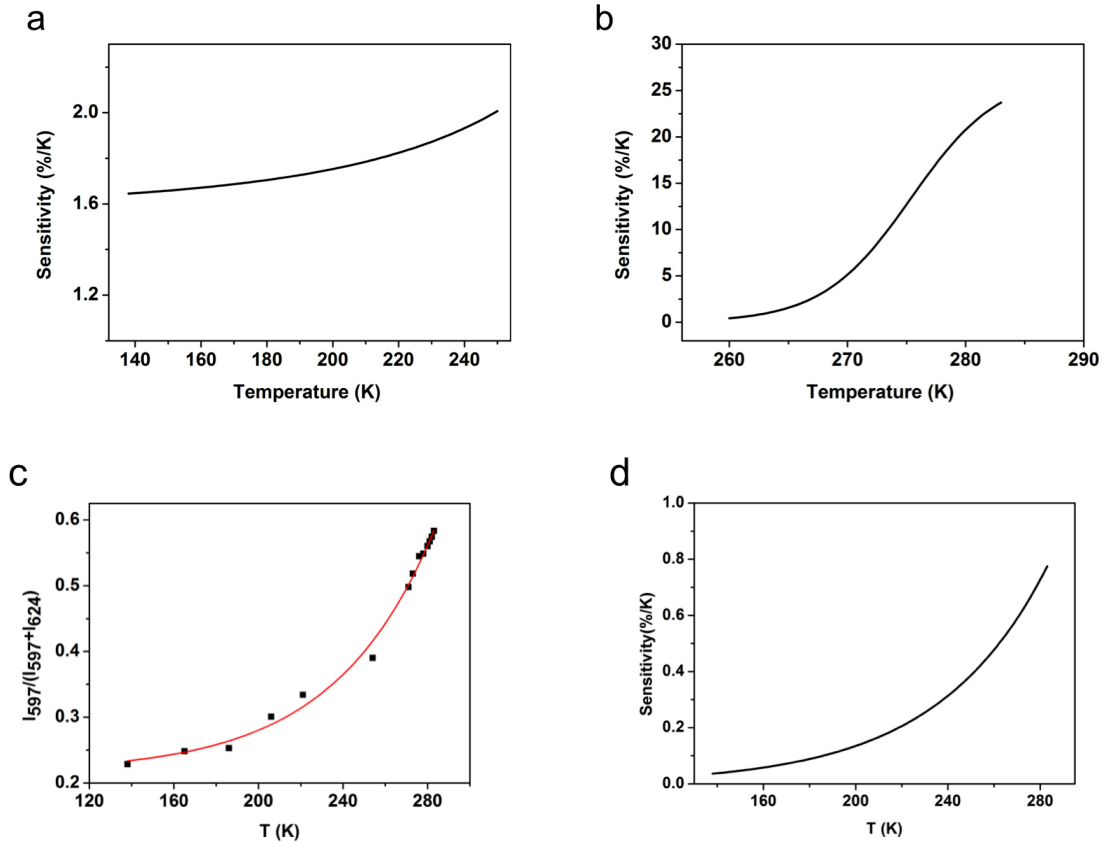


Figure S8. Relative sensitivities and internal sensitivity of MCBD in dioxane. The relative sensitivity (a) from 138 to 250 K, and (b) from 260 to 283 K. (c) The plot of $I_{597}/(I_{597}+I_{624})$ *vs* temperature. (d) Plots of the internal sensitivity versus temperature. S_{int} was calculated according to the equation $S_{int}(T) = |\partial(I_{597}/(I_{597}+I_{624}))/\partial T|$.

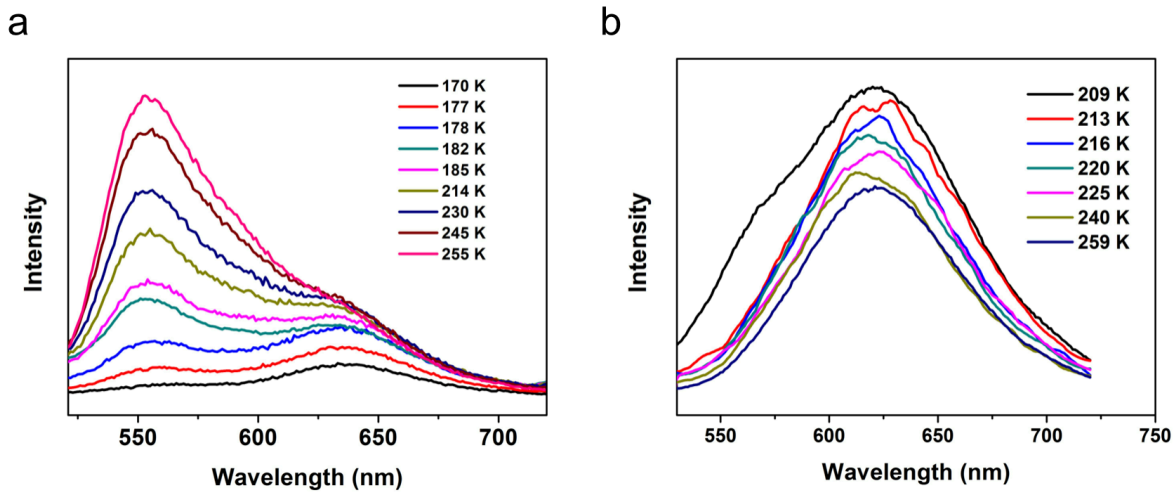


Figure S9. The emission spectra with the temperature changes around the melting points of (a) hexane (b) 1,2-dimethoxyethane.

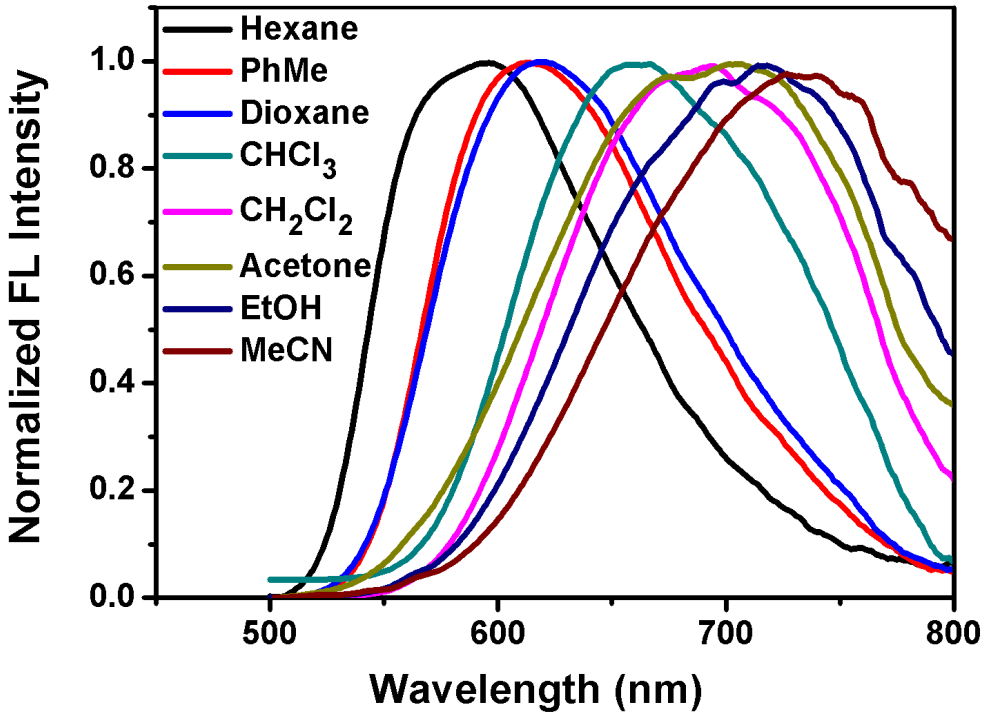


Figure S10. Normalized fluorescence spectra of MCBD in solvents with different polarity.

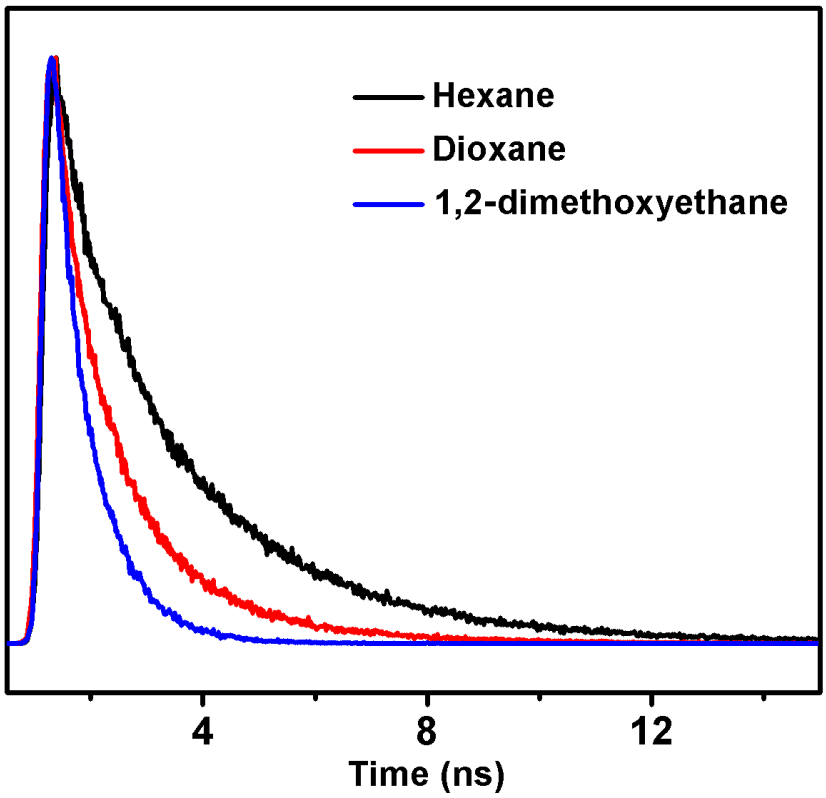


Figure S11. Fluorescence decay curves of MCBD in the three solvents at room temperature.

Table S1 Fluorescence lifetimesof MCBD in the three solvents at room temperature.

Solutions	$\tau_1(f_1)$ / ns	$\tau_2(f_2)$ / ns	χ^2	τ_{avr} / ns
Hexane	1.04(0.15)	2.74(0.85)	1.038	2.49
Dioxane	0.81(0.45)	2.00(0.55)	1.198	1.47
1,2-dimethoxyethane	0.69(1.00)	None	1.259	0.69

Monitor wavelength is 480 nm. The τ_1 andτ_2 are lifetimes (ns), f_1 and f_2 are fractional intensities, and χ^2 is the reduced chi-square, and τ_{avr} is the average lifetime obtained from $f_1\tau_1 + f_2\tau_2$.

Table S2 The comparison between the tabulated and calculated freezing points of common organic solvent.

Solvents	Freezing point (K)	
	Tabulated	Measured
Ethanol	159	160
Acetone	178	180
Ethyl acetate	189	190
Chloroform	209	210
Acetonitrile	228	230

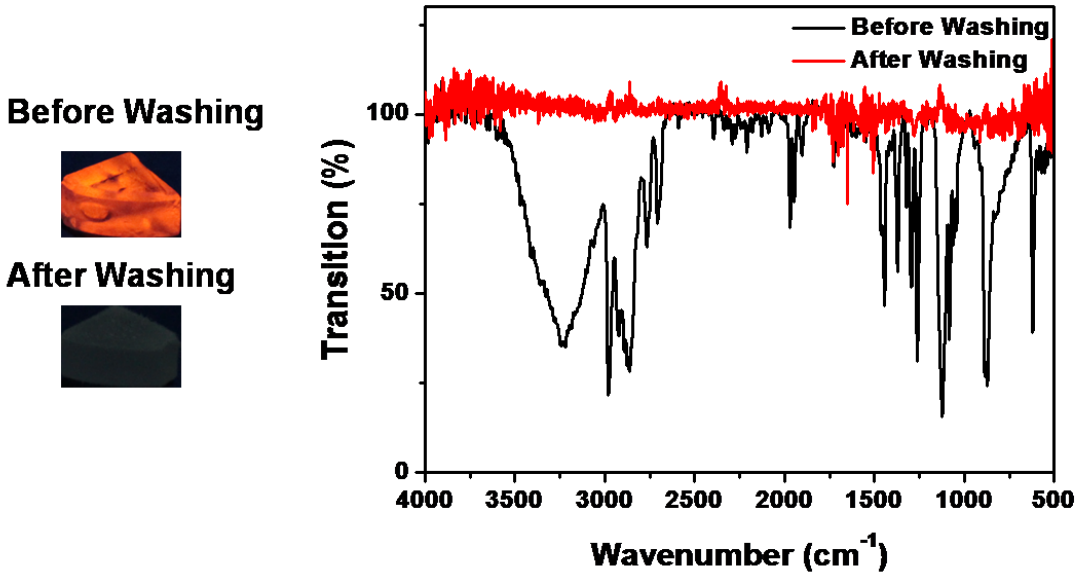


Figure S12. Photos under UV light and FT-IR spectra of KBr crystal wrapped with MCBD dioxane solution before and after washing.

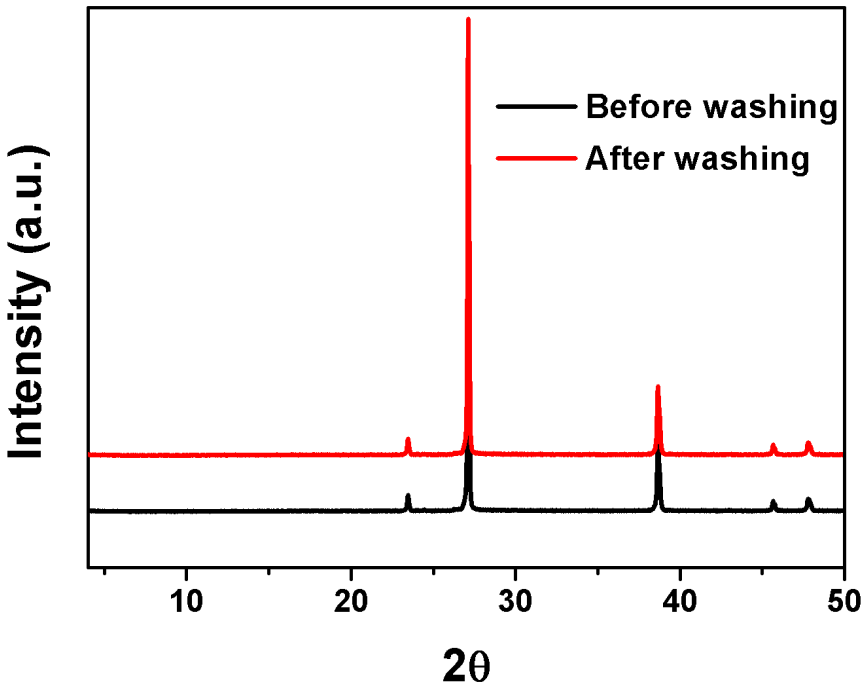


Figure S13. PXRD of KBr crystal wrapped with MCBD dioxane solution before and after washing.

Section D. Supporting references

1. Frisch, M. J. et al.Gaussian 03, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.