

一种新型对苯乙炔基苯衍生物：荧光行为与传感应用

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A New Type of 1,4-Bis(phenylethynyl)benzene Derivatives: Optical Behavior and Sensing Applications

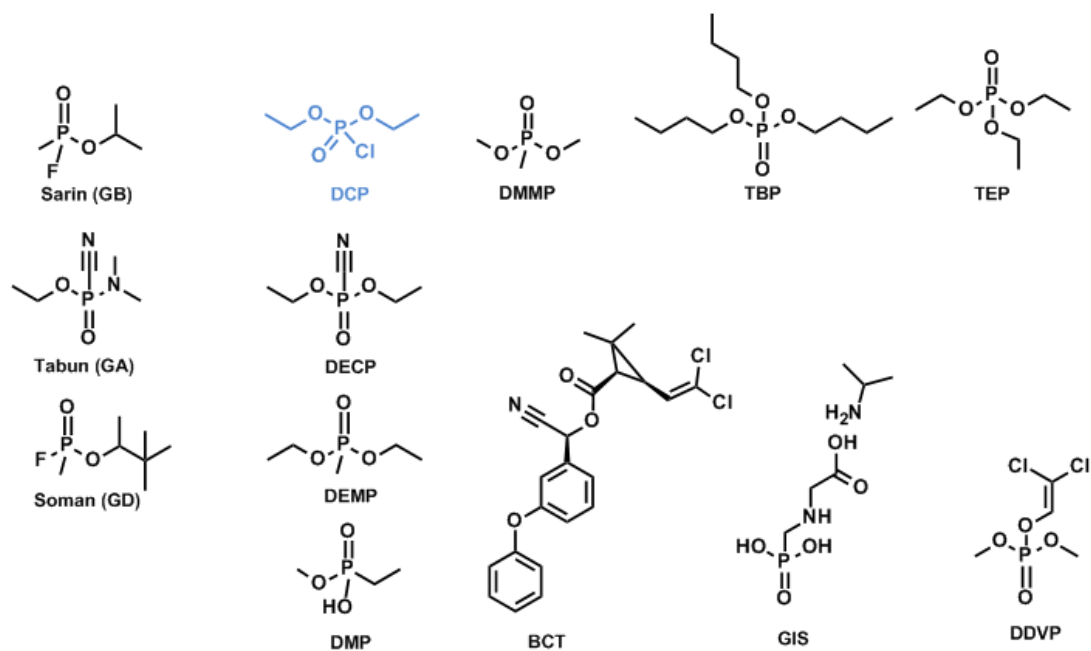
QI Yan-Yu SUN Xiao-Huan CHANG Xing-Mao KANG Rui

LIU Kai-Qiang FANG Yu*

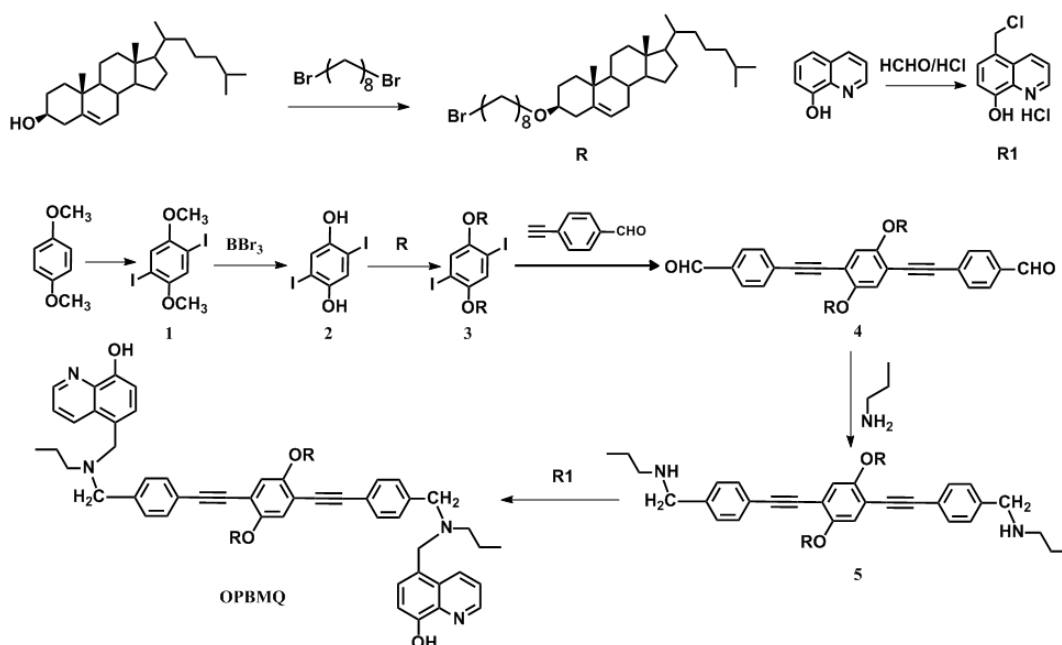
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1. Supplementary Figures and Schemes



Scheme S1. Structures of G-series nerve agents, their simulants (DCP, a simulant of Sarin) and some organophosphorus pesticides



Scheme S2. Schematic representation of the synthesis route of OPBMQ

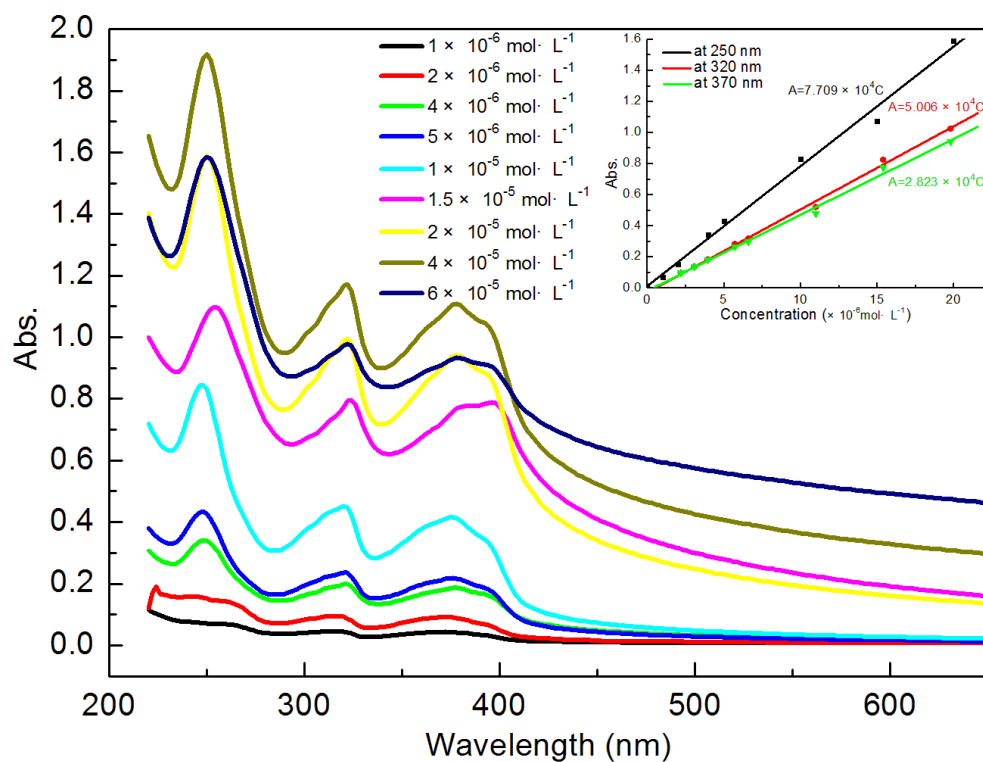


Fig.S1 UV-vis absorptions of OPBMQ in aqueous solution recorded at different concentrations. The inset shows the plots of the absorption intensities against concentrations of OPBMQ, and the data listed aside are the corresponding molar extinction coefficients.

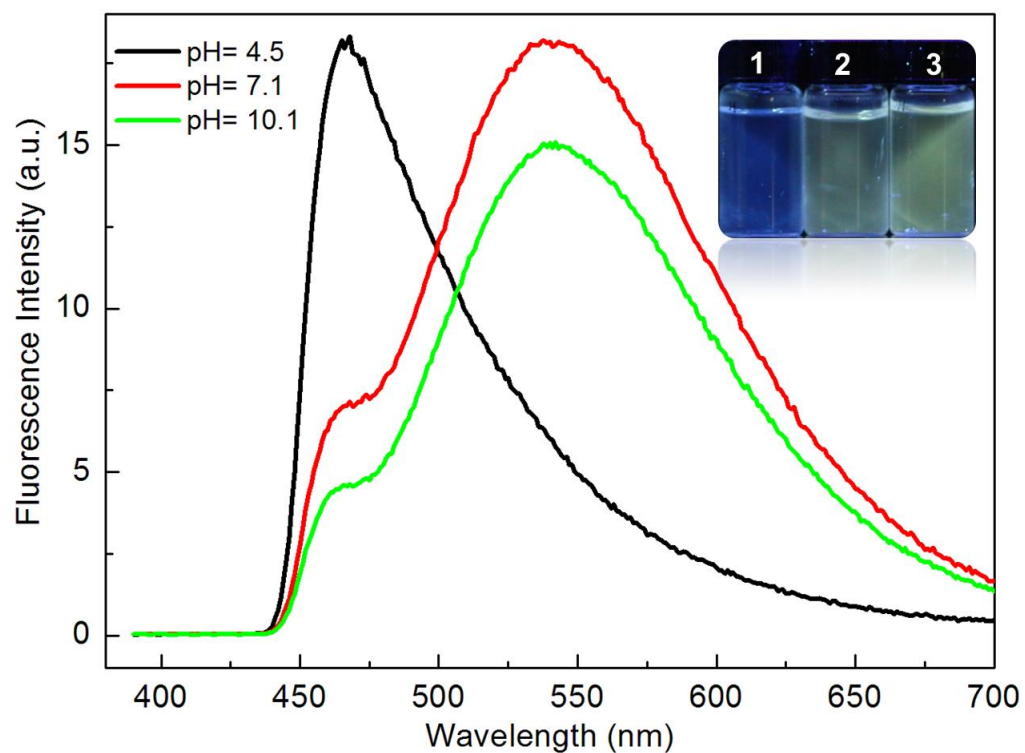


Fig.S2 The effect of pH on the fluorescence behavior of OPBMQ. Inset is the photos of the corresponding solutions, where **1** stands for the system with a pH of 4.5. **2** that of 7.1. and **3** that of 10.1.

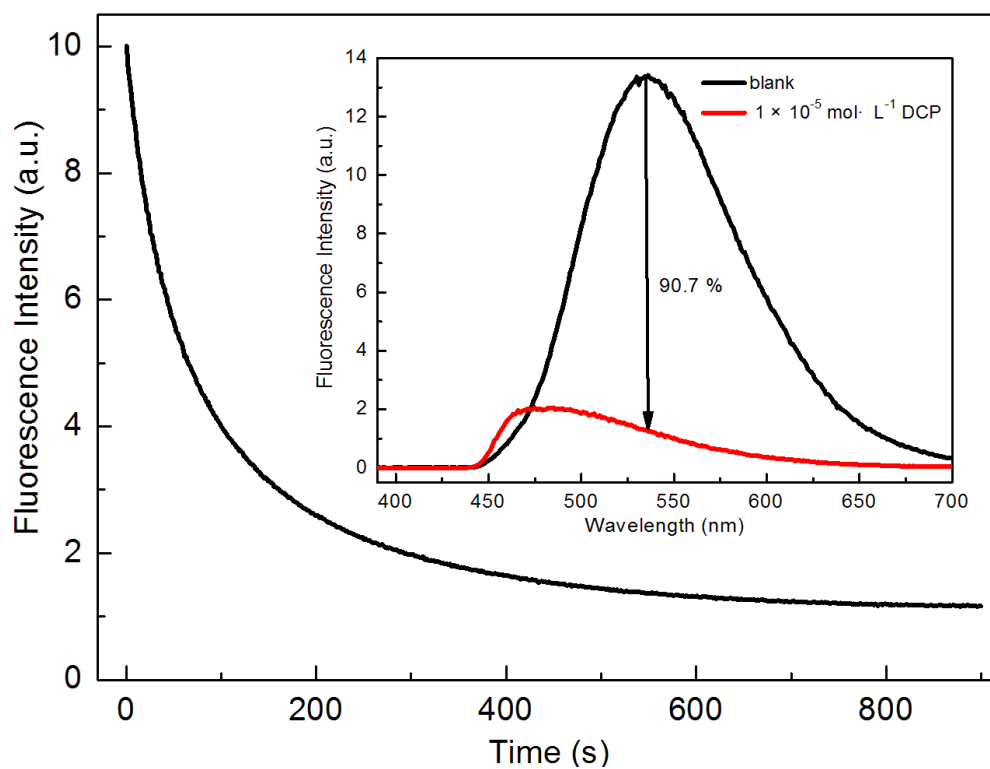


Fig.S3 The time-dependent quenching efficiency of an aqueous solution of OPBMQ ($1 \times 10^{-6} \text{ mol L}^{-1}$) added with $1 \times 10^{-5} \text{ mol L}^{-1}$ DCP. The monitored wavelength was set at 540 nm. Inset: Fluorescence emission spectra before and after (900 s) addition of $1 \times 10^{-5} \text{ mol L}^{-1}$ DCP.

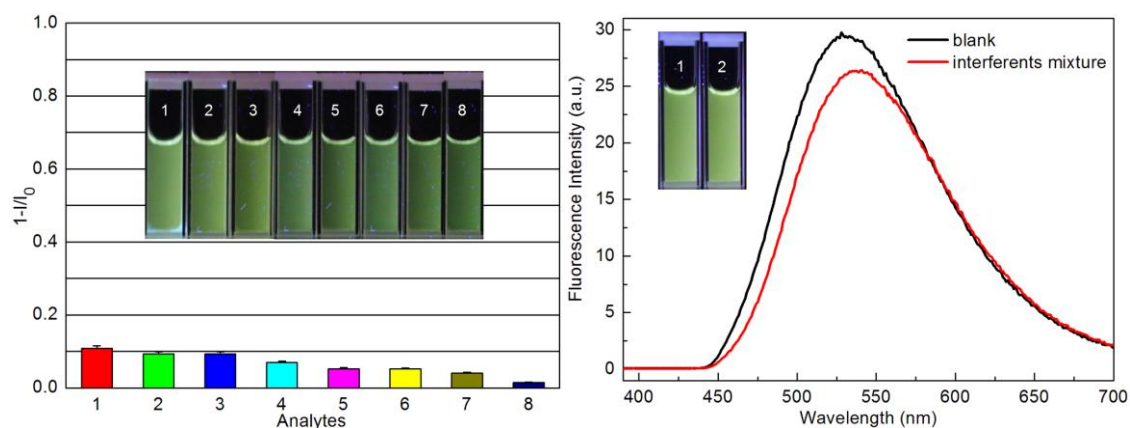


Fig.S4 Quantitative histograms of the fluorescence response of OPBMQ (1×10^{-6} mol L $^{-1}$, $\lambda_{\text{ex}}/\lambda_{\text{em}}=370$ nm/540 nm) to the presence of different amines: Number 1 to 8 represents 1×10^{-5} mol L $^{-1}$ of phenylamine, ethanediamine, diethylamine, hydrazine, diethylenetriamine, propylamine, ammonia, and trimethylamine, respectively. The inset is the images of the relevant solutions under UV light.

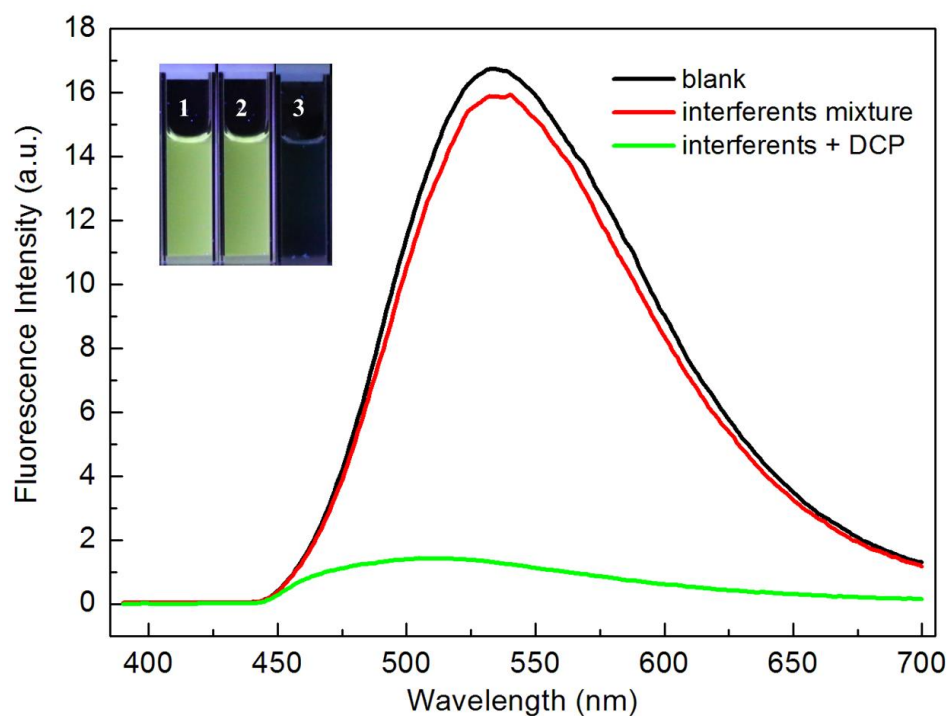


Fig.S5 Fluorescence response of OPBMQ ($1 \times 10^{-6} \text{ mol L}^{-1}$) upon addition of a mixture of all interferents (TBP, DECP, TEP, DMMP, DMP, DEMP, GIS, DDVP, BCT, $1 \times 10^{-5} \text{ mol L}^{-1}$ for each) and the mixture plus DCP ($1 \times 10^{-5} \text{ mol L}^{-1}$) in aqueous phase. The inset is the optical images of (1) blank, (2) interferents alone, and (3) interferents + DCP, respectively.

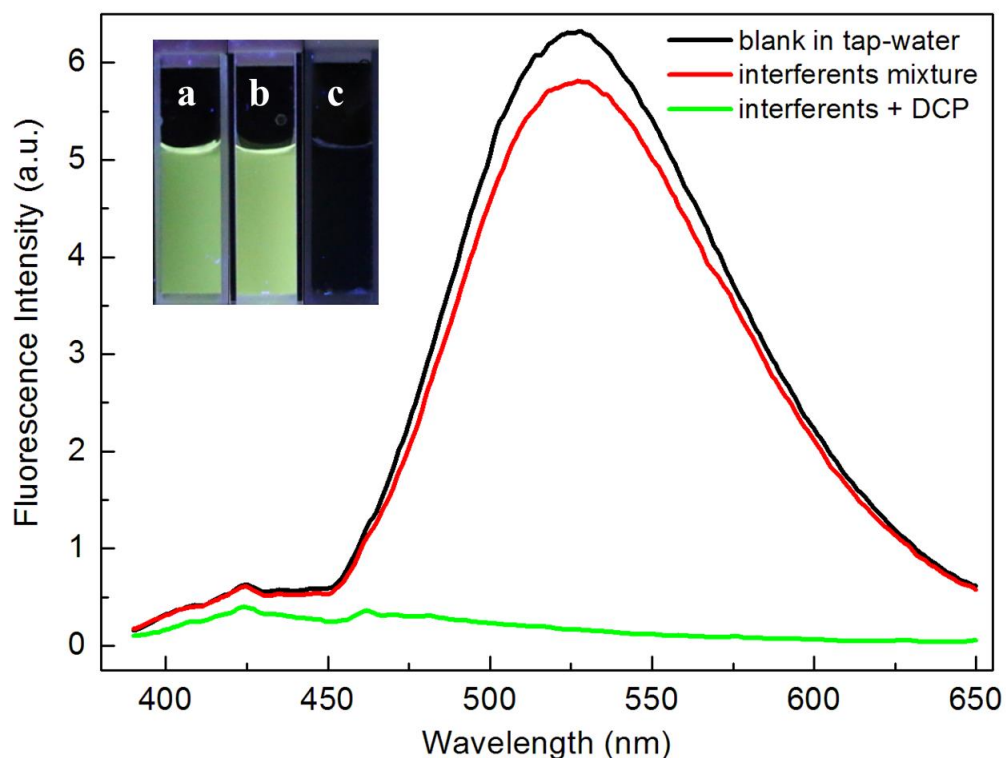


Fig.S6 Fluorescence response of OPBMQ ($1 \times 10^{-6} \text{ mol L}^{-1}$) upon addition of a mixture of all interferents (TBP, DECP, TEP, DMMP, DMP, DEMP, GIS, DDVP, BCT, $1 \times 10^{-5} \text{ mol L}^{-1}$ for each) and the mixture plus DCP ($1 \times 10^{-5} \text{ mol L}^{-1}$) in tap-water. The inset is the optical images of (1) blank in tap-water, (2) interferents alone, and (3) interferents + DCP, respectively.

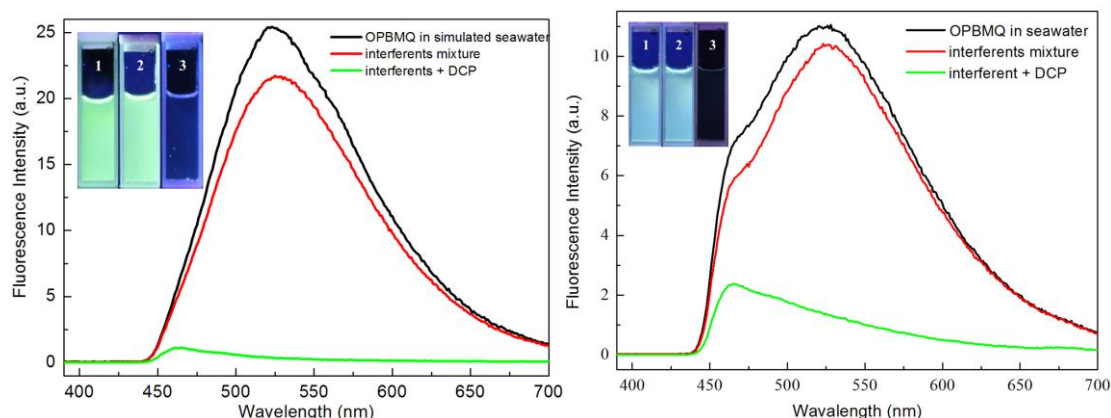


Fig.S7 Fluorescence response of OPBMQ ($1 \times 10^{-6} \text{ mol L}^{-1}$) upon addition of a mixture of all interferents (TBP, DECP, TEP, DMMP, DMP, DEMP, GIS, DDVP, BCT, ammonia, propylamine, diethylenetriamine, ethanediamine, phenylamine, hydrazine, diethylamine and triethylamine, $1 \times 10^{-5} \text{ mol L}^{-1}$ for each) and the mixture plus DCP ($1 \times 10^{-5} \text{ mol L}^{-1}$) in water (Left: simulated seawater; Right: seawater from Southern Sea around Shenzhen, China). The inset is the optical images of (1) blank in simulated seawater or seawater, (2) interferents alone, and (3) interferents + DCP, respectively.

Note: The simulated seawater was prepared by adopting a literature composition and method¹.

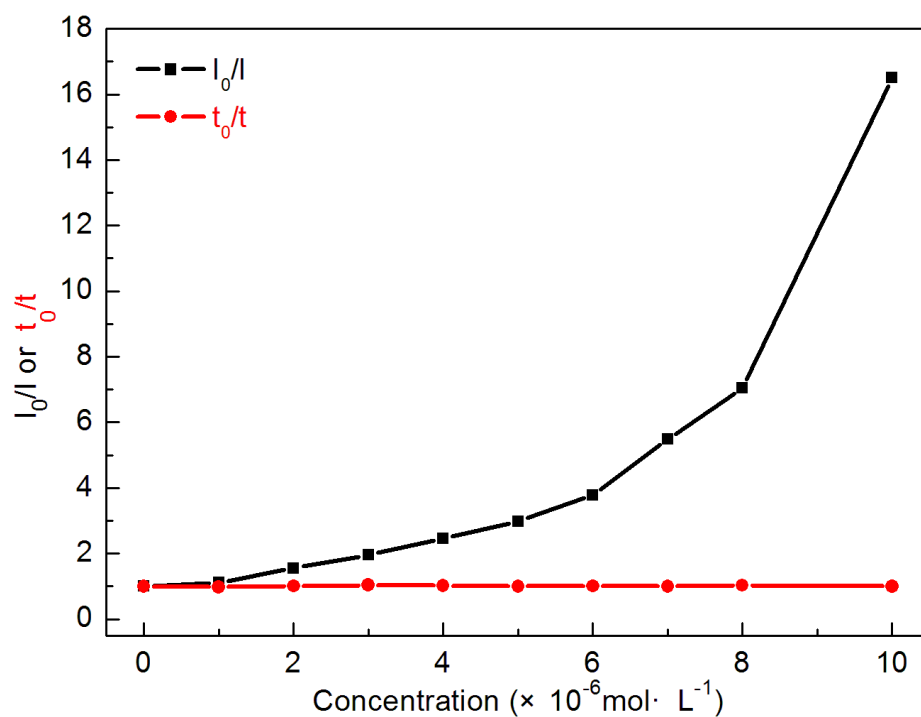


Fig.S8 Plots of I_0/I and τ_0/τ of OPBMQ against the concentration of DCP ($1 \times 10^{-6} \text{ mol L}^{-1}$, $2 \times 10^{-6} \text{ mol L}^{-1}$, $3 \times 10^{-6} \text{ mol L}^{-1}$, $4 \times 10^{-6} \text{ mol L}^{-1}$, $5 \times 10^{-6} \text{ mol L}^{-1}$, $6 \times 10^{-6} \text{ mol L}^{-1}$, $7 \times 10^{-6} \text{ mol L}^{-1}$, $8 \times 10^{-6} \text{ mol L}^{-1}$, and $1 \times 10^{-5} \text{ mol L}^{-1}$).

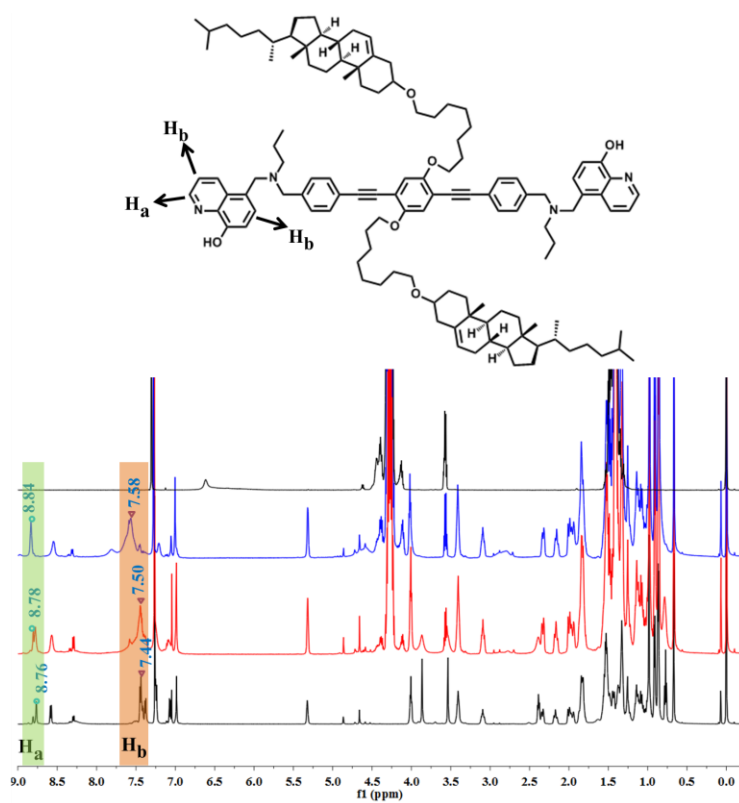


Fig.S9 ^1H NMR titration results for the OPBMQ+DCP system in CDCl_3 solution. Note: From bottom to top, the ratio of OPBMQ : DCP is 1:0, 1:1, 1:2, 0:1, respectively.

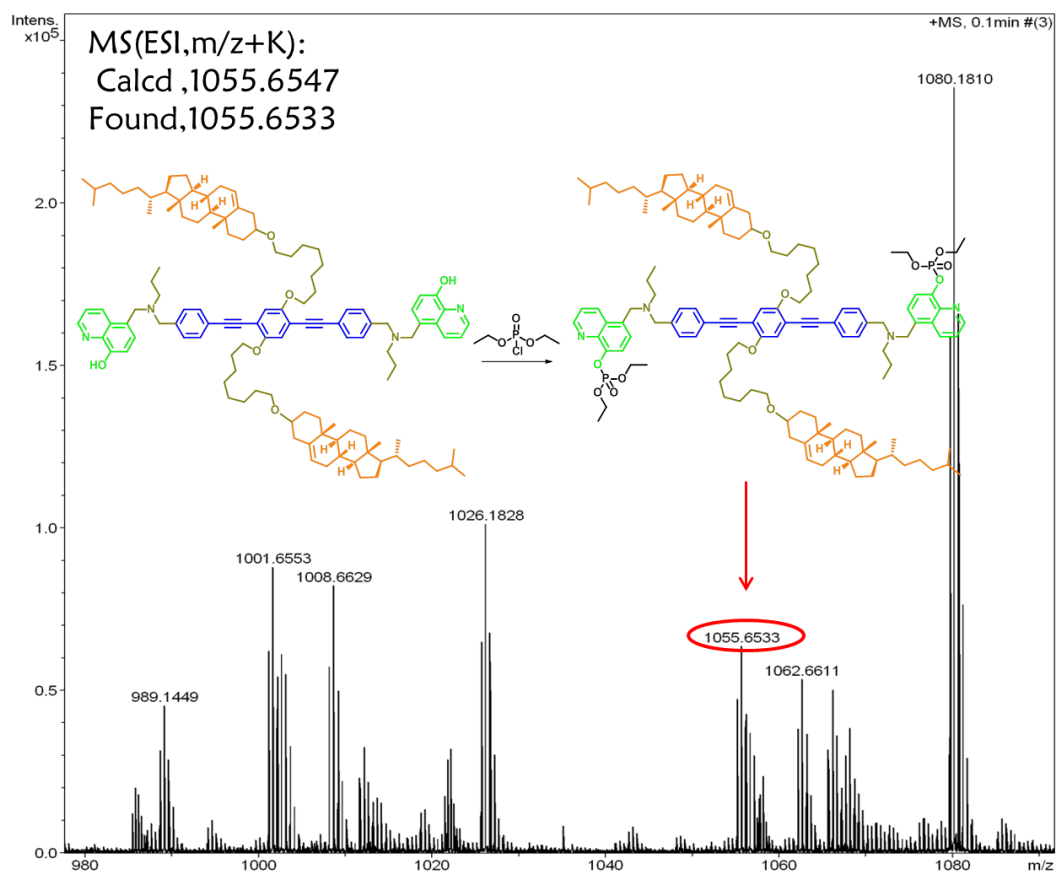


Fig.S10 ESI-MS of OPBMQ-DCP adduct in reaction medium.

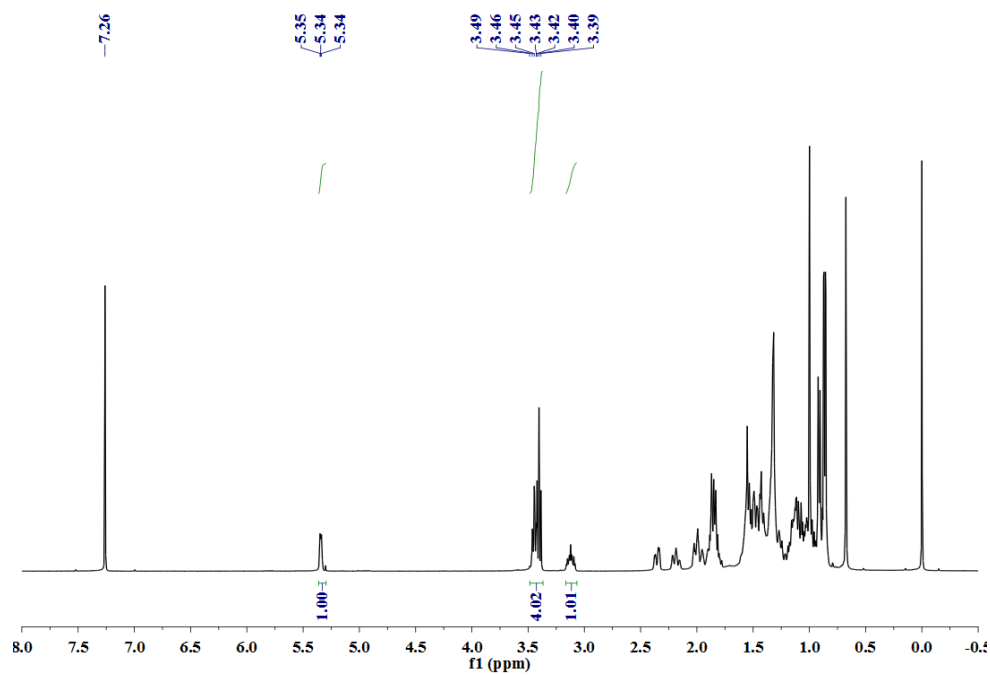


Fig.S11 ¹H NMR spectrum of compound R

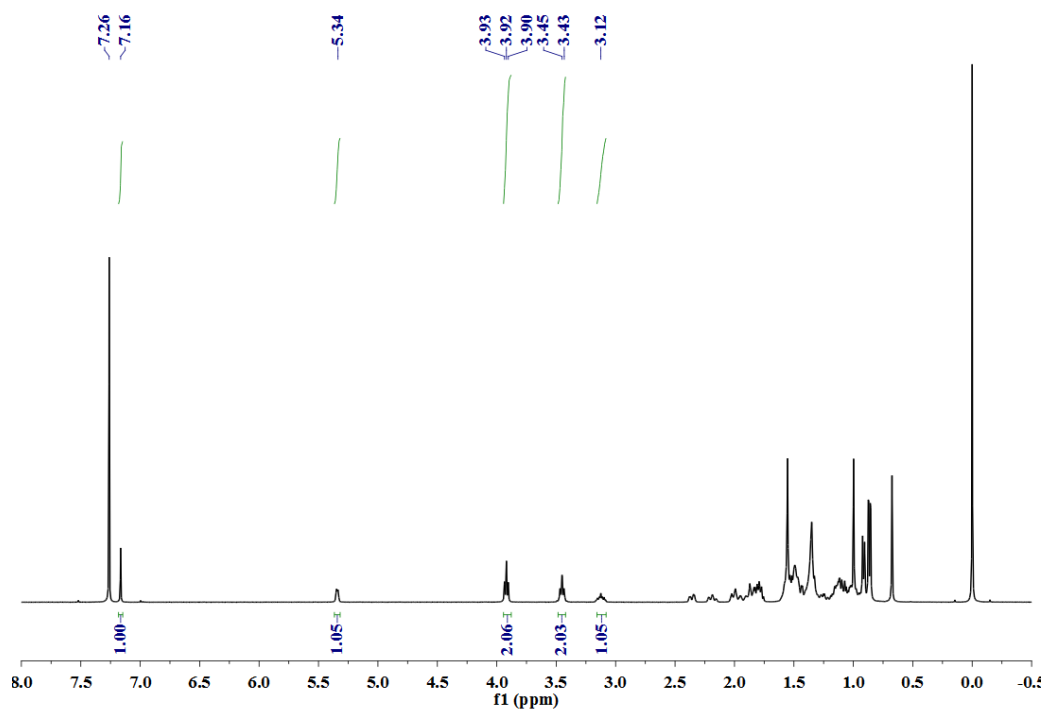


Fig.S12 ¹H NMR spectrum of compound 3

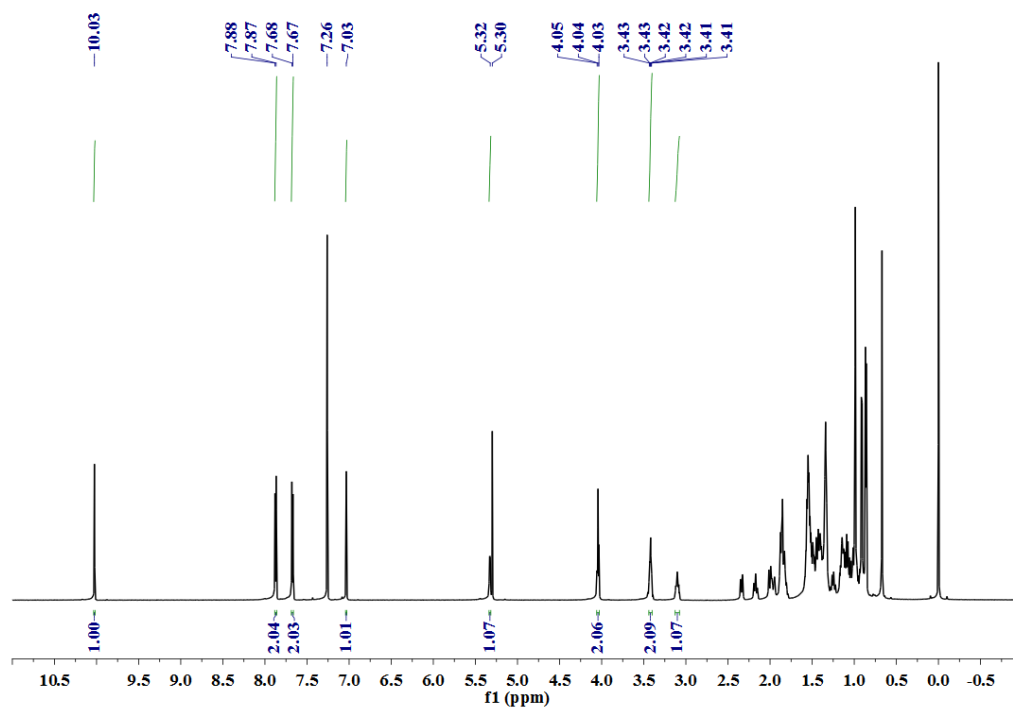


Fig.S13 ¹H NMR spectrum of compound 4

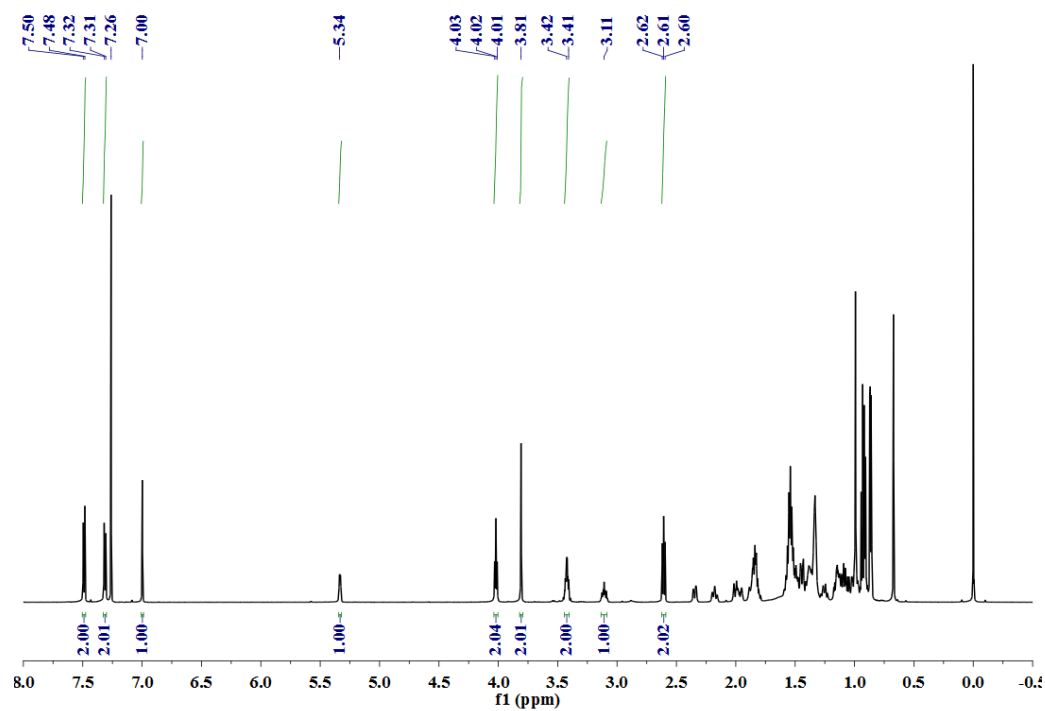


Fig.S14. ¹H NMR spectrum of compound 5

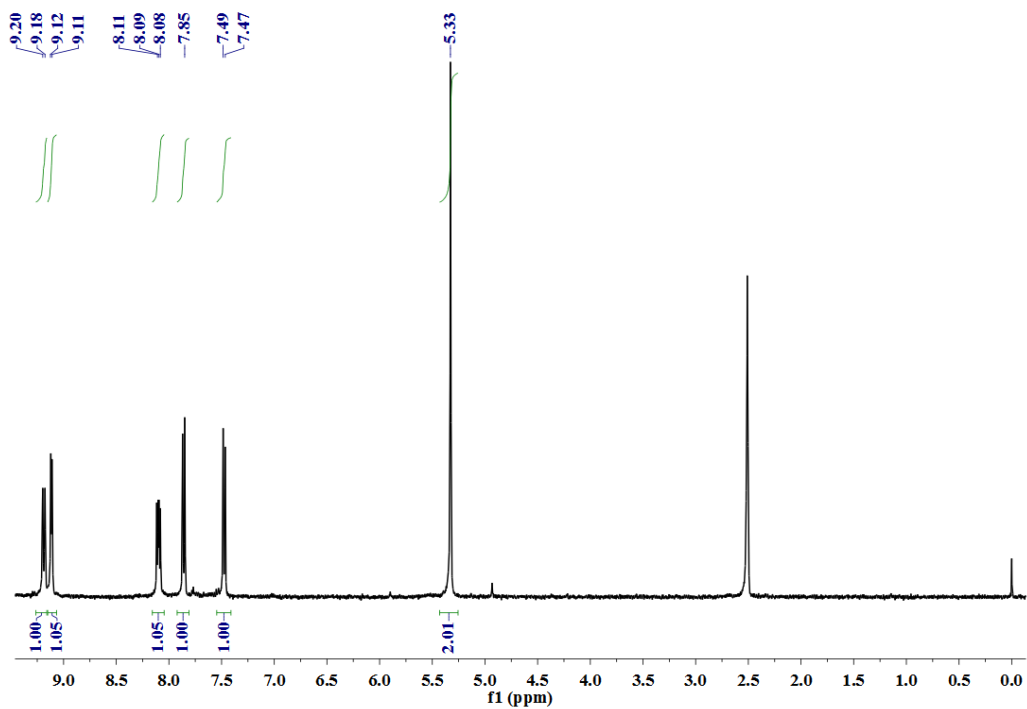


Fig.S15 ^1H NMR spectrum of compound R1

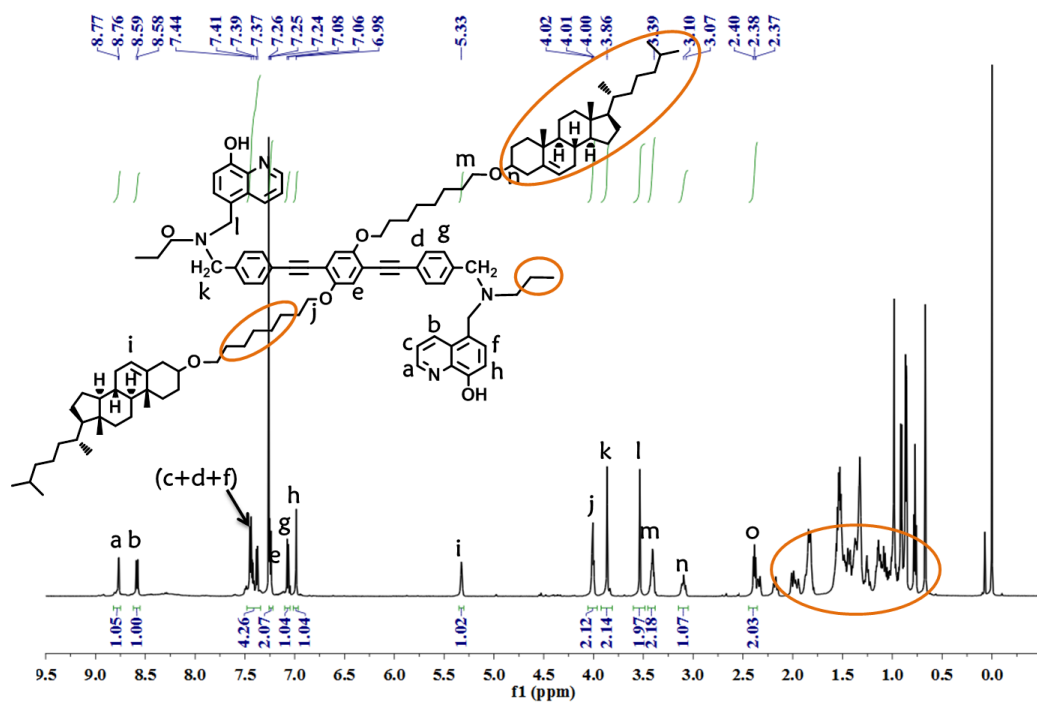


Fig.S16 ^1H NMR spectrum of compound OPBMQ.

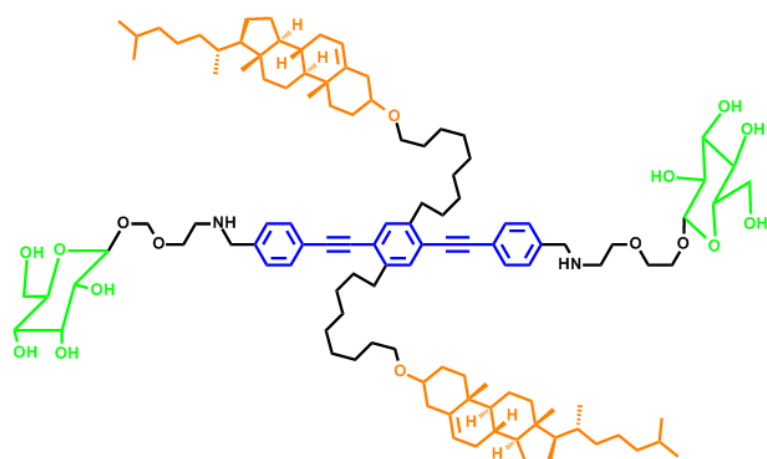


Fig.S17 Molecular structure of the reference compound⁶.

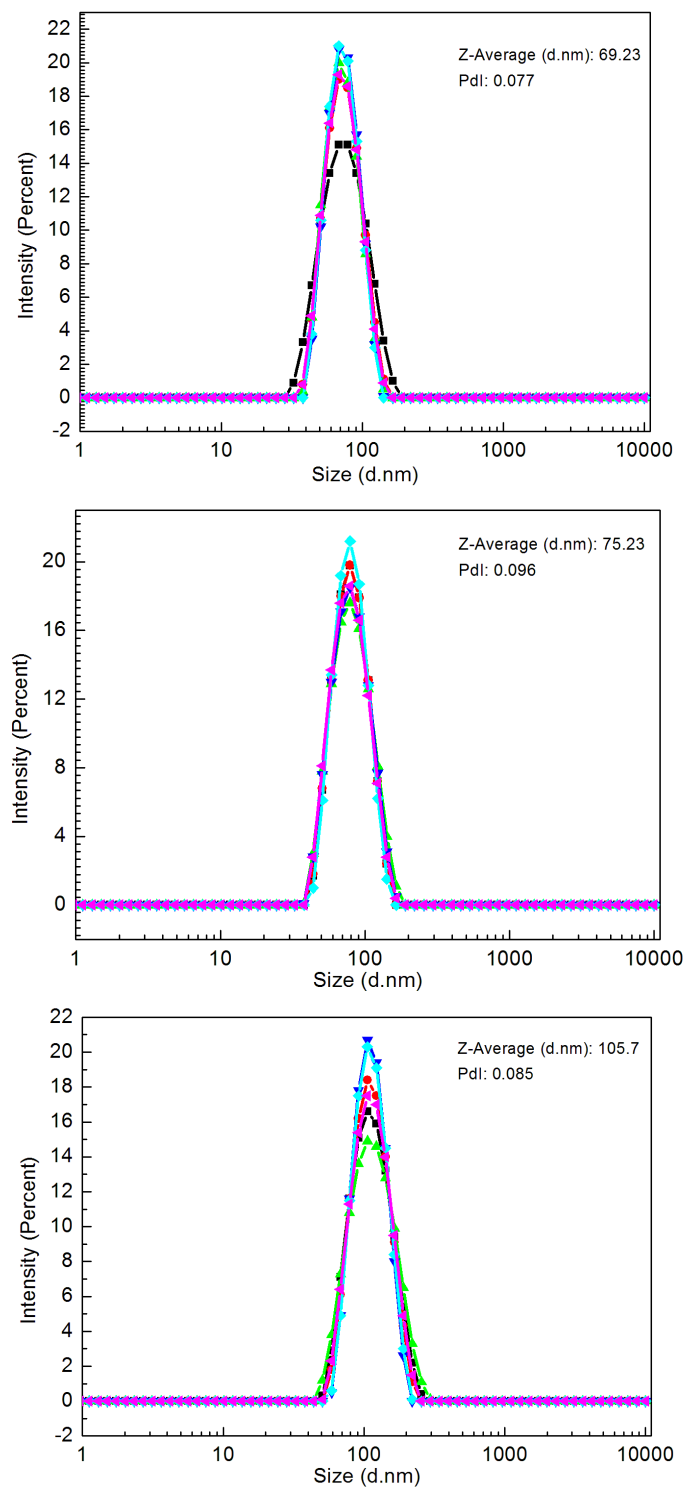


Fig.S18 The Dynamic Light Scattering images of OPBMQ in aqueous solution at a concentration of 1.0×10^{-6} (a), 2.0×10^{-6} (b), 1.0×10^{-5} mol L⁻¹ (c).

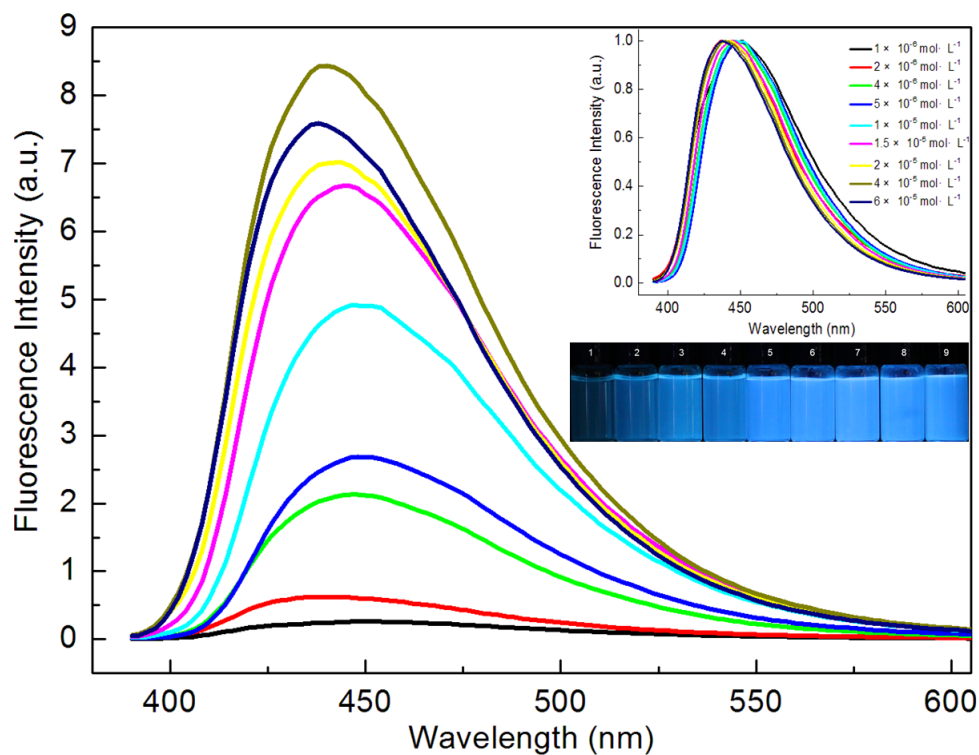


Fig.S19 Fluorescence emission spectra of compound 5 recorded in aqueous solution at different concentrations ($\lambda_{\text{ex}} = 370$ nm). The insets are the normalized fluorescence emission spectra and optical images, where numbers 1 to 9 represent the concentration of 1×10^{-6} , 2×10^{-6} , 4×10^{-6} , 5×10^{-6} , 1×10^{-5} , 1.5×10^{-5} , 2×10^{-5} , 4×10^{-5} , 6×10^{-5} mol L⁻¹, respectively.

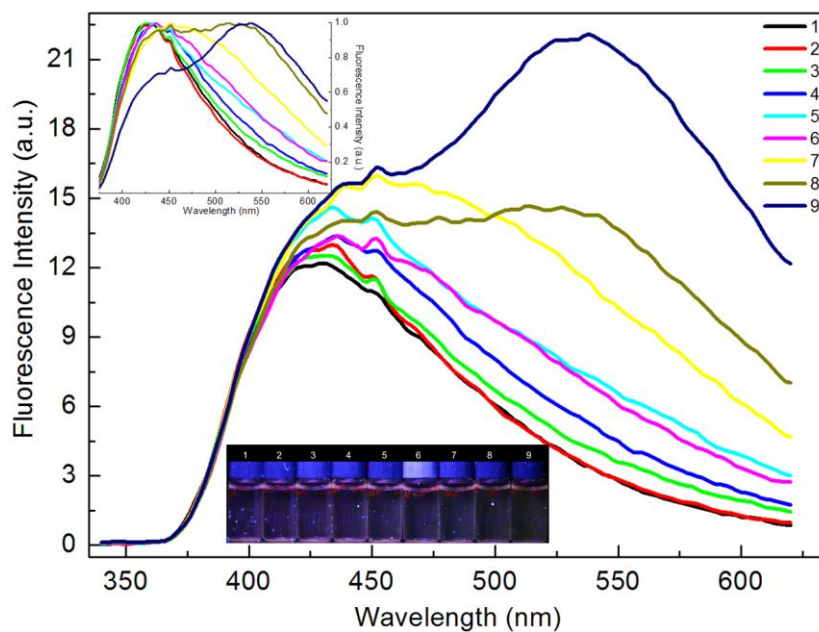


Fig.S20 Fluorescence emission spectra of compound R1 recorded in aqueous solution at different concentrations ($\lambda_{\text{ex}} = 320 \text{ nm}$), where numbers 1 to 9 represent the concentration of 1×10^{-6} , 2×10^{-6} , 4×10^{-6} , 5×10^{-6} , 1×10^{-5} , 1.5×10^{-5} , 2×10^{-5} , 4×10^{-5} , $6 \times 10^{-5} \text{ mol L}^{-1}$, respectively. The insets are the normalized fluorescence emission spectra and optical images.

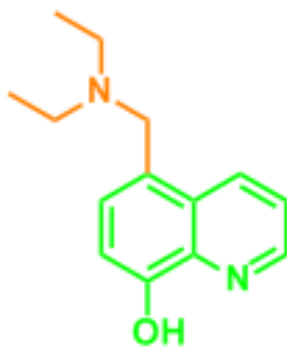


Fig.S21 Molecular structure of the reference compound CMDTA.

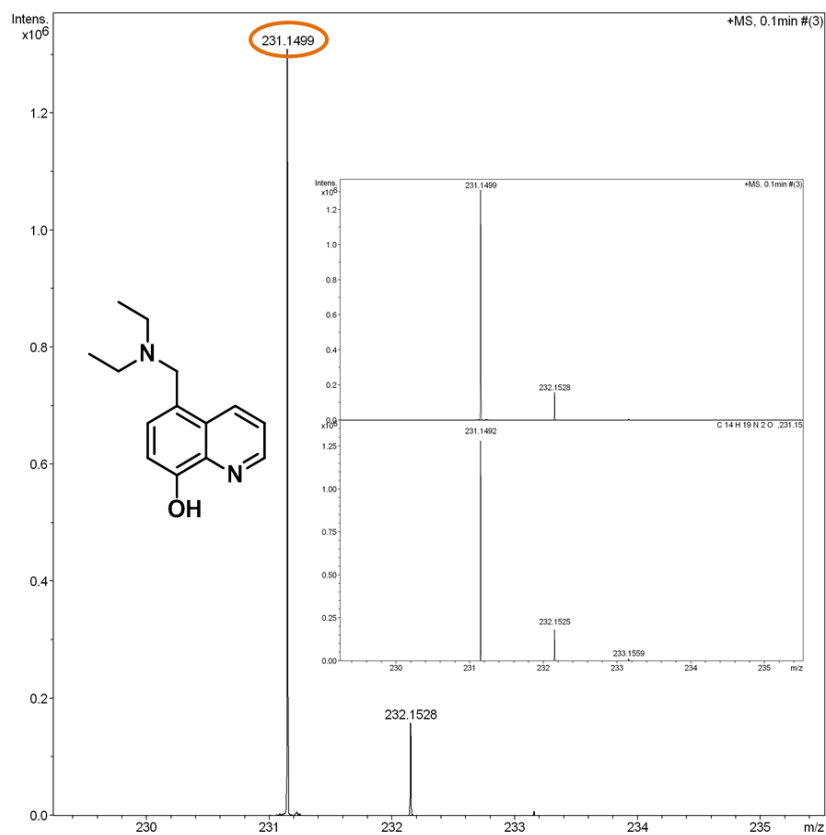


Fig.S22 ESI-MS traces of CMDTA.

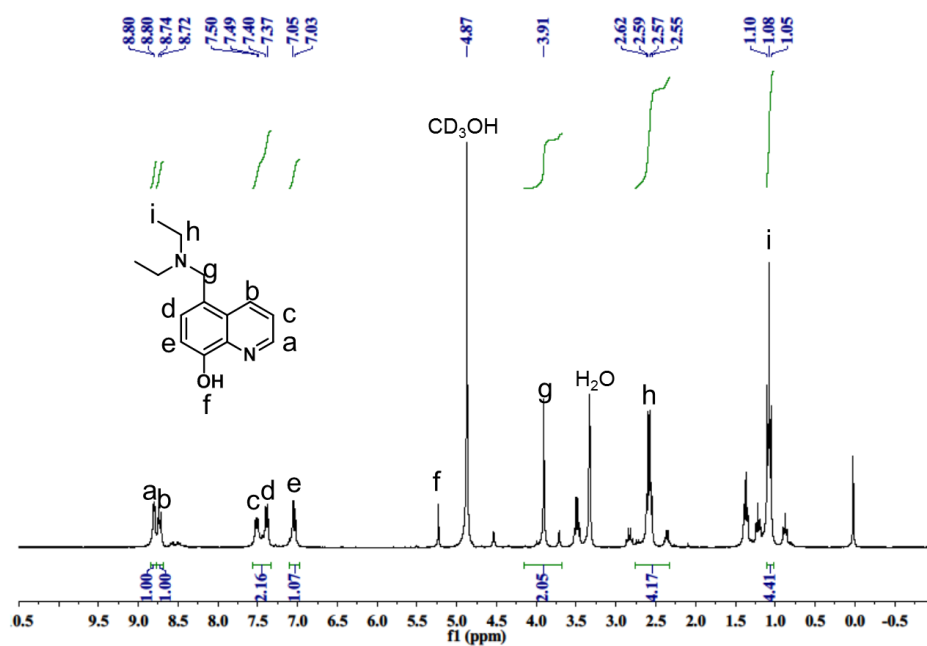


Fig.S23 ¹H NMR spectrum of CMDTA.

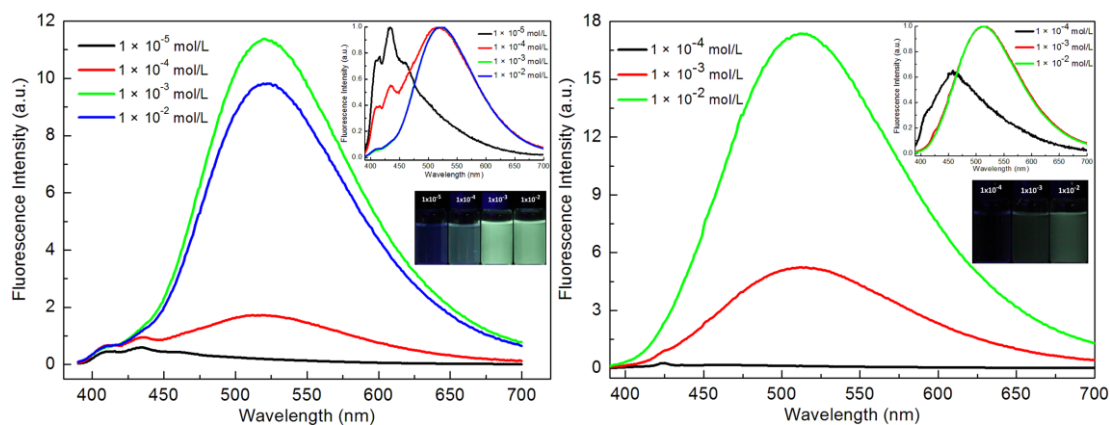


Fig.S24 Fluorescence emission spectra of CMDTA recorded at different concentrations in solution phase (Left: in methanol; Right: in water) ($\lambda_{\text{ex}} = 370$ nm). The inset is the normalized fluorescence emission spectra and optical images of the corresponding solutions.

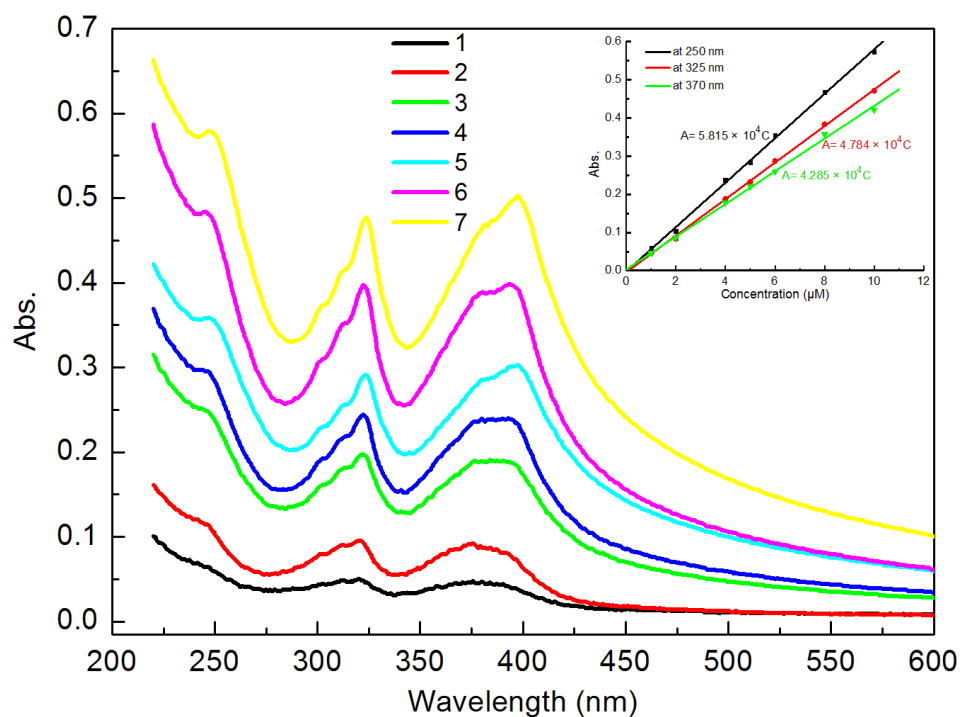


Fig.S25 UV-vis absorptions of compound 5 in aqueous solution recorded at different concentrations. The inset shows the plots of the absorption intensities against concentrations of compound 5, and the data listed aside are the corresponding molar extinction coefficients.

Numbers 1 to 7 represent the concentration of 1×10^{-6} , 2×10^{-6} , 4×10^{-6} , 5×10^{-6} , 6×10^{-6} , 8×10^{-6} , 1×10^{-5} mol L⁻¹, respectively.

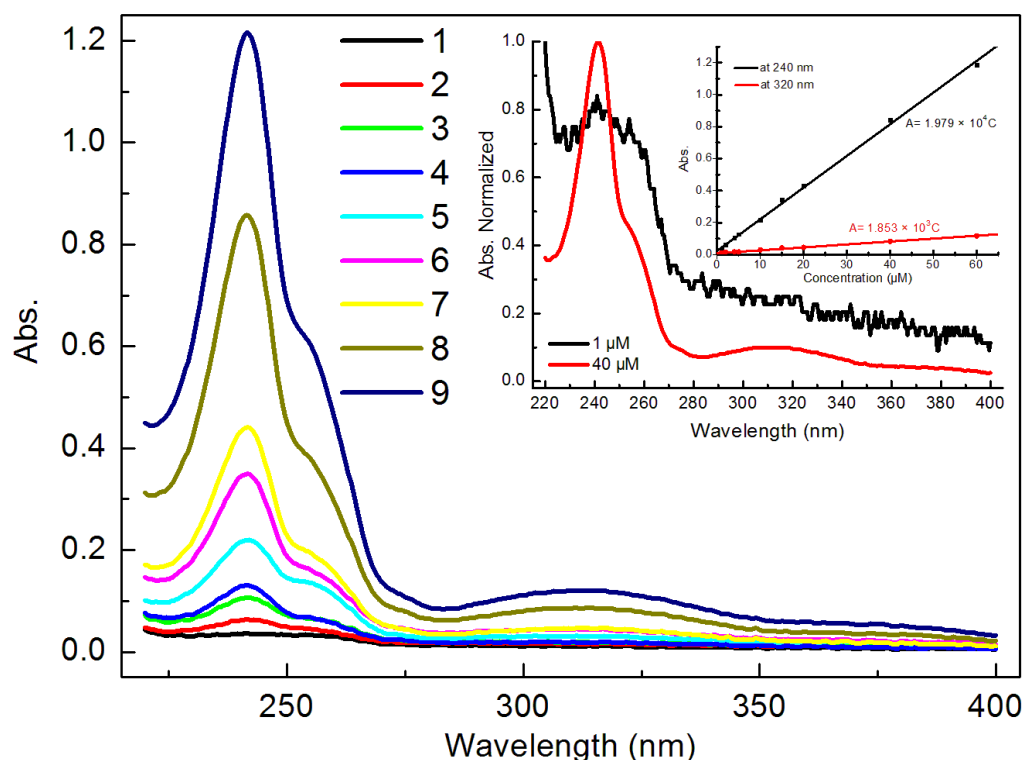
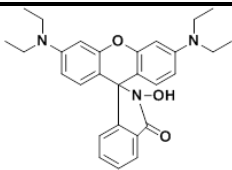
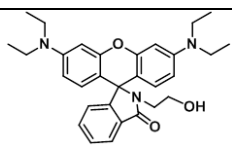
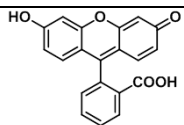
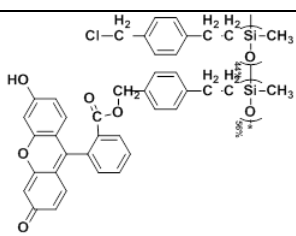
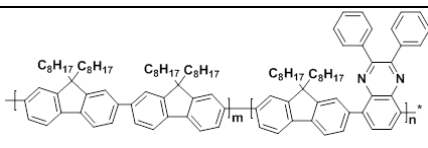
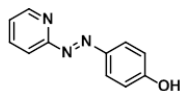
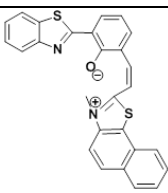
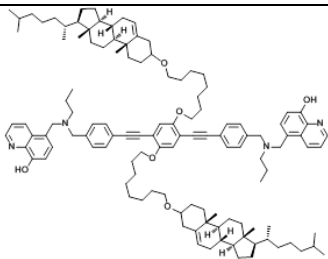


Fig.S26 UV-vis absorptions of compound R1 in aqueous solution recorded at different concentrations. The inset shows the plots of the absorption intensities against concentrations of compound R1, and the data listed aside are the corresponding molar extinction coefficients.

Numbers 1 to 9 represent the concentration of 1×10^{-6} , 2×10^{-6} , 4×10^{-6} , 5×10^{-6} , 1×10^{-5} , 1.5×10^{-5} , 2×10^{-5} , 4×10^{-5} , $6 \times 10^{-5} \text{ mol L}^{-1}$, respectively.

Table S1. Summary of representative fluorescent probes for DCP

No	Phase	Probe	Detection Limit	Solvent	Literature
1	Solution		25000 ppb	DMF	<i>Chem. Commun.</i> , 2010 , 46, 8413-8415
2	Solution		25000 ppb	DMF	<i>Analyst</i> , 2012 , 137, 3224–3226
3	Solution		16.4 ppb	DMSO	<i>Proc. of SPIE Vol.</i> 8710 87100H, 1-5
4	Solution		12 ppb	H ₂ O	<i>Chem. Commun.</i> , 2014 , 50, 9965-9968
5	Solution		1.25 ppb	CH ₃ CH ₂ OH	<i>ACS Appl. Mater. Interfaces</i> , 2014 , 6, 22884–22893
6	Solution		0.53 ppb	CH ₃ CN	<i>Adv. Funct. Mater.</i> , 2011 , 21, 4035–4040
7	Solution		0.017 ppb	Aqueous DMSO (3 : 7 v/v)	<i>Chem. Commun.</i> , 2015 , 51, 9729–9732
8	Solution		1×10^{-9} mol L ⁻¹	Aqueous THF (100:1 v/v)	This Work
			0.56 pg/cm ²	Paper Strips	

Note: the system (Aqueous THF (100:1 v/v)) used in this work was described at 2.10 Preparation of Solutions in Experiment Section in this Supporting Information.

Table S2. Photophysical parameters of OPBMQ and the two reference compounds, including the UV-vis absorptions (*Abs.*), the molar extinction coefficients (ϵ), the maximum emission wavelength (*Em*), the fluorescent quantum yield (Φ), and the fluorescent lifetime (τ).

Compound	<i>Abs.</i> (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	<i>Em</i> (nm)	Φ_{FI}	τ (ns)
OPBMQ	250	7.709 × 10 ⁴	445 540	50.4%	1.80
	320	5.006 × 10 ⁴			
	370	2.823 × 10 ⁴			
5	250	5.815 × 10 ⁴	450	64.5%	2.16
	325	4.784 × 10 ⁴			
	370	4.285 × 10 ⁴			
R1	240	1.980 × 10 ⁴	430	14.2%	1.28
	320	1.853 × 10 ³	530		

Video S1. The video of DCP monitoring by using a prototype device.

2. Experimental section

2.1 Materials and reagents

1,4-Dimethoxybenzene (TCI, 99%), 4-ethynylbenzaldehyde (Alfa aesar, 99%), propylamine (Aladdin, 98%), 8-hydroxyquinoline (Aladdin, 98%), Pd (PPh₃)₄ (Alfa aesar, 99%) and CuI (Alfa aesar, 98%) were used as received. DCP, DECP, tributyl phosphate (TBP), triethyl phosphate (TEP) and dimethyl phosphate (DMP) are of analytical grade and were bought from Aladdin. Dimethyl methylphosphonate (DMMP) was bought from MAYA Reagent. DEMP was bought from Heowns Biochem Technologies LLC (Tianjin, China). All the reagents are of, at least, analytical grade and used without further purification. The preparation of the compounds was conducted using standard vacuum line and Schlenk technique under a purified argon atmosphere. DMF and dichloromethane were distilled from calcium hydride under argon prior to use. Methanol was distilled from magnesium under argon before use. THF and toluene was distilled from sodium benzophenone ketyl under argon prior to use. Water used in this work was acquired from a Milli-Q reference system except those specially specified.

2.2 Measurements and characterization

¹H NMR and ¹³C NMR spectra were acquired on Bruker AV 400 NMR and 600 NMR spectrometer at room temperature. Pressed KBr disks for the powder samples were used for the transmission infrared (FT-IR) spectroscopy measurements, and their FT-IR spectra were measured on a Bruker VERTEX 70v spectrometer. The MS were collected on a Bruker maxis UHR-TOF mass spectrometer in ESI positive mode. Melting point measurement was conducted on X-5 Microscopic melting point meter (Beijing Tech Instrument). Optical photos were carried out on a Canon 70D camera. DLS measurement was conducted on a Malvern Zeta Sizer Nano-ZS90. The pH was measured by a Leinuo pH meter. Fluorescence measurements were performed at room temperature on a time-correlated single photon counting Edinburgh Instruments FLS 920 fluorescence spectrometer.

2.3 Synthesis of Compound R

A mixture of cholesterol (6 g, 15.5 mmol), 1,8-dibromooctane (14.29 mL, 77.5 mmol), KOH (3.48 g, 62 mmol) and dry THF (50 mL) was stirred under argon at 80

°C for 48 h. The solution was concentrated, the residue was diluted with CH₂Cl₂ (50 mL), washed with brine (50 mL), and then dried over MgSO₄. The MgSO₄ was removed by vacuum filtration, and the filtrate was evaporated. The methanol (100 mL) was added to the resulting yellow oil and stirred for 1 h. Then sucked out the supernatant fluid and added methanol (100 mL), stirred for 1 h again. Repeat the above operation for 3 times, the white solid was obtained. Finally, the resulting white solid was purified by column chromatography on silica gel column with petroleum ether: CH₂Cl₂ (v:v, 1:1) as eluent to afford compound R as white solid (6.34 g, 70%). Melting point: 68-70 °C. IR (KBr, cm⁻¹): 2931, 2855, 1461, 1381, 1103. ¹H NMR (Fig.S11, δ ppm, 400 MHz, CDCl₃): 5.33 (s, 1H), 3.49-3.39 (m, 4H), 3.12 (m, 1H), 2.34-0.68 (m, 55H).

2.4 Synthesis of Compound 3

A mixture of compound R (2 g, 3.5 mmol), 2,5-diiodobenzene-1,4-diol (0.5 g, 1.4 mmol)², KOH (0.63 g, 11.2 mmol) and dry DMF (30mL) was stirred under argon atmosphere at 160 °C for 48 h. Then, the reaction mixture was poured onto water (400 mL), and resulted in white solid precipitate. The residue was collected, washed with water, dried and purified by column chromatography on silica gel column with petroleum ether: CH₂Cl₂ (v:v, 2:3) to afford compound 3 as white solid (1.5 g, 75%). Melting point: 149-151 °C. IR (KBr, cm⁻¹): 2931, 2855, 1461, 1355, 1263, 1110. ¹H NMR (Fig.S12, δ ppm, 400 MHz, CDCl₃): 7.16 (s, 1H), 5.34 (s, 1H), 3.92-3.90 (m, 2H), 3.47-3.43 (m, 2H), 3.10-3.12 (m, 1H), 2.38-0.67 (m, 55H). Anal. Calcd. for C₇₆H₁₂₄O₄I₂: C, 67.34; H, 9.22; Found: C, 66.99; H, 9.50.

2.5 Synthesis of Compound 4³

To a solution of diisopropylamine (6 mL) in toluene (14 mL) were added compound 3 (500 mg, 0.37 mmol), 4-ethynylbenzaldehyde (144 mg, 1.1 mmol), Pd(PPh₃)₄ (21.3 mg, 0.018 mmol), and CuI (3.5 mg, 0.018 mmol). The reaction mixture was stirred under argon at 70 °C for 48 h, then diluted with CH₂Cl₂ (50 mL), and then washed with brine (50 mL), finally dried over MgSO₄. The MgSO₄ was removed by vacuum filtration, and the filtrate was evaporated to dryness. The resulting yellow oil was stirred with acetone overnight, the resulting yellow solid was

obtained by vacuum filtration, then purified by column chromatography on silica gel column with CH₃OH : CH₂Cl₂ (v:v, 1:100) to afford compound 4 as pale green solid (yield 72%). Melting point: 120-122 °C. IR (KBr, cm⁻¹): 2931, 2852, 2721, 2208, 1705, 1601, 1461, 1381, 1213. ¹H NMR (Fig.S13, δ ppm, 400 MHz, CDCl₃): 10.0 (s, 1H), 7.88-7.87 (d, 2H), 7.68-7.67 (d, 2H), 7.03 (s, 1H), 5.32 (s, 1H), 4.05-4.03 (m, 2H), 3.43-3.41 (m, 2H), 3.12-3.10 (m, 1H), 2.34-0.67 (m, 55H). MS: (m/z, [M+Na]⁺): calculated: 1382.02, Found: 1382.97.

2.6 Synthesis of Compound 5

A mixture of 4 (0.20 g, 0.14 mmol) and propylamine (120 μL, 1.4 mmol) was dissolved in dichloromethane. The reaction mixture was stirred under argon at 45 °C for 48 h. After cooling to room temperature, NaBH₄ (0.1 g, 2.6 mmol) was added and stirred for another 2 h. Then, the reaction mixture was diluted with dichloromethane, washed with brine and then dried over MgSO₄. The MgSO₄ was removed by vacuum filtration, and the filtrate was evaporated to dryness. The resulting pale yellow solid was purified by column chromatography on a silica-gel column with dichloromethane: methanol (v:v, 50:1). A pale yellow solid was obtained (0.18 g, 85%). Melting point: 133-135 °C. ¹H NMR (Fig.S14, δ ppm, 600 MHz, CDCl₃): 7.50-7.48 (d, 2H), 7.33-7.32 (d, 2H), 7.00 (s, 1H), 5.34 (s, 1H), 4.03-4.01 (t, 2H), 3.81 (s, 2H), 3.43-3.41 (t, 2H), 3.12-3.08 (t, 2H), 2.62-2.60 (t, 2H), 2.37-0.68 (m, 46H). IR (KBr, cm⁻¹): 3395, 3033, 2938, 2860, 2208, 1522. MS (ESI, m/z): Calcd for [(M+H)⁺]: 1447.2879, Found: 1447.2865.

2.7 Synthesis of Compound R1

R1 was synthesized according to a literature method, and characterized by a ¹H NMR technique (Fig.S15)⁴.

2.8 Synthesis of Compound OPBMQ

A mixture of 5 (0.50 g, 0.35 mmol), R1 (0.18 g, 0.77 mmol) and K₂CO₃ (0.68 g, 4.9 mmol) was dissolved in dichloromethane. The reaction mixture was stirred under argon at 45 °C for 48 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane, washed with brine and then dried over MgSO₄. The MgSO₄ was removed by vacuum filtration, and the filtrate was evaporated to dryness. A pale yellow solid was obtained (0.45 g, 73%). Melting point: 60-62 °C. ¹H NMR (Fig.S16, δ ppm, 600 MHz, CDCl₃): 8.77-8.76 (d, 1H), 8.59-8.58 (d, 1H), 7.44-7.37 (m, 4H), 7.25-7.24 (d, 2H), 7.08-7.06 (d, 1H), 6.98 (s, 1H), 5.33 (s, 1H), 4.02-4.00 (t,

2H), 3.86 (s, 2H), 3.54 (s, 2H), 3.40-3.39 (d, 2H), 3.10-3.07 (m, 1H), 2.40-2.37 (m, 2H), 2.35-0.68 (m, 46H). IR (KBr, cm^{-1}): 3395, 3033, 2938, 2860, 2208, 1522. MS (ESI, m/z): Calcd for $[\text{M}^{2+}+\text{H}]$: 881.1493, Found: 881.1503. Anal. calcd. for OPBMQ ($\text{C}_{120}\text{H}_{166}\text{N}_4\text{O}_6$): C 81.86, H 9.50, N 3.18, Found: C 81.87, H 9.65, N 3.01.

2.9 Synthesis of Compound CMDTA⁵

CMDTA was synthesized according to a literature method, and characterized by ESI-MS and ^1H NMR techniques (Fig.S21, S22).

2.10 Preparation of Solutions

OPBMQ Solutions: Stock solution of ($1 \times 10^{-3} \text{ mol L}^{-1}$) OPBMQ was prepared by dissolving 0.00898g of OPBMQ in 5 mL THF. We make a $1 \times 10^{-4} \text{ mol L}^{-1}$ THF solution from a $1 \times 10^{-3} \text{ mol L}^{-1}$ stock by a 10x dilution, which is also the stock solution. All other testing solutions of 6.0×10^{-5} to $1.0 \times 10^{-6} \text{ mol L}^{-1}$ OPBMQ aqueous solutions recorded were prepared by dilution the stock solution ($1 \times 10^{-3} \text{ mol L}^{-1}$ and $1 \times 10^{-4} \text{ mol L}^{-1}$), ensuring that the volume of THF was one percent of the total volume, of which the others are water (Milli-Q water, tap-water, simulated seawater, seawater). The solutions using in solvent effect studies were prepared by using the corresponding solvent instead of water to dilute the stock solution ($1 \times 10^{-4} \text{ mol L}^{-1}$).

Buffer Solutions: The $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer solution was made by mixing a Na_2CO_3 solution (0.1 mol L^{-1} , 6 mL) and a NaHCO_3 solution (0.1 mol L^{-1} , 4 mL), and the pH of the solution was determined to be 10.1. A NaCl solution (0.1 mol L^{-1}) was adopted as a buffer with a pH of 7.1. The acidic buffer (pH=4.5) was a solution of NaAc and HAc (NaAc , 0.2 mol L^{-1} , 4.9 mL; HAc , 0.2 mol L^{-1} , 5.1 mL).

Organophosphate Solutions: The stock solution of ($2.5 \times 10^{-3} \text{ mol L}^{-1}$) DCP was prepared by diluting 3.613 μL of DCP to 10 mL Milli-Q water or tap-water. The solutions of all other organophosphate nerve agents and pesticides were prepared in a similar way, but the volumes of them are different (TEP: 4.248 μL , 41%GIS: 27.827 μL , DMMP: 2.709 μL , DEMP: 3.653 μL , DMP: 2.360 μL , 4.5% BCT: 174.693 μL , DECP: 3.793 μL , 77.5% DDVP: 5.024 μL , TBP: 6.800 μL).

Amines Solutions: The stock solution of ($2.5 \times 10^{-2} \text{ mol L}^{-1}$) ammonia was prepared by diluting 4.81 μL of the solution to 10 mL with Milli-Q water, tap-water, simulated seawater, or real seawater. We make a $2.5 \times 10^{-3} \text{ mol L}^{-1}$ solution from a $2.5 \times 10^{-2} \text{ mol L}^{-1}$ stock by a 10 times dilution, which is the solution to be detected. The

solutions of all other amines solutions were prepared in a similar way, but the volumes of them are different (propylamine: 10.30 μL , diethylenetriamine: 13.44 μL , ethanediamine: 8.35 μL , phenylamine: 11.39 μL , Hydrazine: 6.05 μL , diethylamine: 12.88 μL , trimethylamine: 17.33 μL).

CMDTA Solutions: Stock solution of (1 mol L^{-1}) CMDTA was prepared by dissolving 1.15152 g of CMDTA in 5 mL methanol. We make a $1 \times 10^{-2} \text{ mol L}^{-1}$ methanol solution from a 1 mol L^{-1} stock by a 100 times dilution, which is also the stock solution. Other methanol solutions of CMDTA was made by 10 times dilution of $1 \times 10^{-2} \text{ mol L}^{-1}$. The aqueous solutions of CMDTA was made by 100 times dilution of 1 mol L^{-1} stock solution, ensuring that the volume of methanol was one percent of the total volume, of which the others are water.

2.11 Detection of Nerve Agent Simulants

Under the excitation of 370 nm, the fluorescence spectrum of OPBMQ in aqueous solution (2.5 mL, $1.0 \times 10^{-6} \text{ mol L}^{-1}$) was measured in quartz cell (1.0 cm) at room temperature. Then, DCP in aqueous solution (1 μL , $2.5 \times 10^{-3} \text{ mol L}^{-1}$) was added into the cell. After mixing for 5 min, the emission spectrum was recorded. Quenching test was conducted via introduction of the DCP solution, of which 1 μL of the solution each time. The test was repeated for nine times. The tests for other chemicals were performed in the same way.

2.12 Detection of Amines

Under the excitation of 370 nm, the fluorescence spectrum of OPBMQ in aqueous solution (2.5 mL, $1.0 \times 10^{-6} \text{ mol L}^{-1}$) was measured in quartz cell (1.0 cm) at room temperature. Then, ammonia or the organic amines in aqueous solution (10 μL , $2.5 \times 10^{-3} \text{ mol L}^{-1}$) was added into the cell. After mixing for 5 min, the emission spectrum was recorded. Finally, DCP in aqueous solution (10 μL , $2.5 \times 10^{-3} \text{ mol L}^{-1}$) was added into the cell. After mixing for 5 min, the emission spectrum was recorded.

2.13 ^1H NMR Titration

^1H NMR titration was carried out on a Bruker AV 600 NMR spectrometer at room temperature. In the experiment, the stock solution of the probe was prepared by dissolving 11 mg OPBMQ in CDCl_3 (namely, $6.25 \times 10^{-6} \text{ mol}$ per 0.5 mL). And meanwhile the solution of DCP was prepared by diluting 22.58 μL DCP with CDCl_3 (namely, $1.5625 \times 10^{-4} \text{ mol}$ per 0.5 mL). Then the solution of DCP was added to the

solution of OPBMQ to make the ratio of OPBMQ to DCP increase from 1:0 to 1:1 and 1:2 in mole to mole. At the same time, 30 μL of DCP was diluted by 0.5 mL CDCl_3 and to record its own ^1H NMR spectrum.

2.14 Preparation of Test Strips

Blank test strips were prepared by cutting ordinary filter paper (1.2 cm $\times$ 1.2 cm). The strips as obtained were further treated by immersing them into the THF solution of OPBMQ (1×10^{-3} mol L^{-1}), and then dried in air at room temperature.

2.15 Visualization Test of DCP

The aqueous solutions of DCP with definite concentrations were prepared by diluting its stock solution (1×10^{-2} mol L^{-1}) with Milli-Q water. Then, the DCP solutions as obtained ($5 \times 10^{-11} \sim 1 \times 10^{-2}$ mol L^{-1}) and Milli-Q water were spotted onto the test strips using a glass micro-syringe. In order to ensure consistent analysis, all depositions were prepared from a 1 μL volume, thereby producing a spot of 0.2~0.6 cm in diameter. After evaporation of the solvent at room temperature, the filter paper was illuminated with handheld UV light (365 nm). The dark spots were identified by an independent observer, and each set of experiments was repeated three times for consistency. The detection limits were calculated from the lowest concentration of the solution that enabled an independent observer to detect the quenching visually.

3. The pH Effect on Fluorescence Spectra of OPBMQ

As for fluorescence sensing in aqueous phase, the pH of the solution may play a vital role among the numerous factors and enormously affects the fluorescence of the probe. Taking this point into consideration, a series of fluorescence experiments of the compound were conducted in different solutions of different pH. Fig.S2 shows the fluorescence spectra of OPBMQ (1.0×10^{-6} mol L^{-1}) in acidic (pH 4.5), neutral (pH 7.1) and alkaline (pH 10.1) buffer solutions at room temperature. As is shown in the figure, the emission maxima of the corresponding solutions shifted to longer wavelength distinctly as the pH increased. For example, the maximum emission wavelength was 468 nm at pH 4.5, but it shifted to 542 nm at pH 7.1 or 10.1. Analysis of the inset of the figure reveals that the color of the solutions turned from blue to yellow as the pH from acidic to neutral or alkaline. In other words, the maximum

emission of the probe in neutral or alkaline aqueous solutions is strictly equivalent, but they become slightly different at acidic solution. Therefore, we select the neutral aqueous solution as the sensing medium.

4. Determination of the Detection Limit⁶

4.1 Detection Limit to DCP

The detection limit (DL) of OPBMQ in aqueous solution to DCP has been determined according to the following equations or functions:

$$S_b = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (1)$$

$$S = \frac{\Delta I}{\Delta c} \quad (2)$$

$$DL = \frac{3S_b}{S} \quad (3)$$

Firstly, the standard deviation regarding aqueous solution of OPBMQ (1×10^{-6} mol L⁻¹) and the instrument was determined by measuring the fluorescence intensities (x_i) for more than 10 times, and calculating the corresponding average intensity ($\bar{x}$). By fitting the data into equation (1), the value of standard deviation (S_b) was obtained.

Secondly, we added different amount of DCP (2.5×10^{-3} mol L⁻¹) diluted by water into the above-mentioned aqueous solution of OPBMQ, and then the fluorescence emission intensities were recorded. Corresponding variations in intensity (ΔI) were calculated. By fitting the data into equation (2), where Δc is the variations of DCP concentration, the value of precision S was calculated.

Finally, with the values of S_b and S as determined, the DL for the present system was calculated according to equation (3).

5. Fluorescence and DLS Studies of Reference Systems

Recently, a similar compound (C2, c.f. Fig.S17) was prepared in our lab, concentration-dependent studies revealed that the maximum emission of C2 shifted to

longer-wavelengths along with increasing its concentration, a result rationalized by the aggregation of the fluorescent core, BPEB, of the compound⁶. In fact, this is a rather general phenomenon observed in organic fluorescent aggregates, of which Yao and coworkers had made a great effort and rationalized the phenomenon by proposing a concept of lattice softening effect⁷. Therefore, it was suspected that the spectral change, in particular change in the position, might be a result of the change in the aggregate size. To confirm this conjecture, the aggregation of OPBMQ in aqueous solution was examined via Dynamic Light Scattering (DLS) studies, of which the results were shown in Fig.S18. It is seen that for the solutions of 1×10^{-6} , 2×10^{-6} and 1×10^{-5} mol L⁻¹, the average diameters of the aggregates increased from 69.23, to 75.23 and then to 105.7 nm, a result in support of the explanations.

To reveal the nature of the spectral change upon variation of the compound concentration, compound 5 and R1 (Scheme S2) were chosen as controls. Fig.S19 and S20 depict the concentration-dependent fluorescence emission spectra of compound 5 and R1 in water, respectively. With inspection of Fig.S19, it is clearly seen that no matter what the exact concentration of compound 5, of which BPEB is the core structure, its maximum emission is always around 450 nm. But for R1, of which 8-HQ is the fluorescent center, the position of its maximum emission is highly concentration dependent. For systems with concentrations from 1×10^{-6} mol L⁻¹ to 2×10^{-5} mol L⁻¹, the emission appeared at ~430 nm with 320 nm as the excitation wavelength. The emission, however, shifted to ~530 nm when its concentration exceeded 4×10^{-5} mol L⁻¹. These results demonstrated clearly that why the fluorescence emission of OPBMQ is characterized by two distinct emissions positioning at 445 and 540 nm, respectively. As for why the two emissions show different concentration dependent behaviour, it might be a result of different fluorescence quantum yields that make the inner filtering effect of the two units start from different concentrations and the great aggregation tendency of the fluorescent compound as developed due to presence of the BPEB and Chol structures. Furthermore, these results also demonstrate that introduction of 8-HQ endowed the compound, OPBMQ, an extraordinary optical behaviour in aqueous solution, which lays foundation for finding useful applications.

As discussed already, the core structure of OPBMQ is BPEB, which contains three benzene rings and has strong tendency to form aggregate. In addition, auxiliary structure, Chol should also play positive role for the aggregation due to its

self-assembly property as mentioned earlier. Moreover, the aggregation must be also enhanced due to the hydrophobicity of the two units. As for the observation that 8-HQ lost its fluorescence emission at the concentrations under study possibly due to the excited state intra-molecular proton transfer (ESIPT) or intra-molecular charge transfer (ICT), a non-radiative channel to release their excited state energy⁸⁻¹⁰. But this ICT or ESIPT process could be blocked by complexation with metal ions due to screening of the process. Similarly, the emission may also be enhanced upon increasing their concentrations¹¹. To further confirm this statement, a control compound CMDTA (Fig.S21, see Supporting Information), a simple derivative of 8-HQ, was synthesized according to a literature method, whose characterization results were shown in Fig.S22 and S23⁵. Fluorescence measurements demonstrated that the emission from the aggregate of CMDTA increases along with increasing its concentration (Fig.S24, see Supporting Information). This result may explain why the fluorescence emission of the aqueous solution of OPBMQ is dominated by 8-HQ emission at lower concentrations, but by BPEB moiety at higher concentrations because with the presence of BPEB and cholesteryl units the solubility of OPBMQ should be much lower than that of the reference compound CMDTA, and this may make the aggregation of the 8-HQ unit of OPBMQ start at a significantly lower concentration, resulting in fluorescence emission. With further increasing the concentration of OPBMQ, less emissive BPEB starts to emit, and the emission from 8-HQ is suppressed possibly due to inner-filtering effect. The inner-filtering effect can be clearly seen in the reference system as shown in the concentration-dependent emission spectra of the compound. Anyway, presence of the multiple structural units may make the molecules of the compound adopt a variety of conformations or different aggregate structures, which may explain why OPBMQ shows so colorful fluorescence behavior in different solvents at different concentrations.

6. UV-vis Studies of the Solution Behavior of OPBMQ

To rationalize the argument as described, the UV-vis absorption spectra of OPBMQ were recorded in water at different concentrations ranging from 1×10^{-6} to 6×10^{-5} mol L⁻¹, and the results are shown in Fig.S1. It is seen that the absorption spectra are composed of three bands appearing at ~250 nm, ~320 nm and 370 nm, respectively. With comparison to the absorptions of the two reference compounds 5 and R1 (c.f. Scheme S2, Fig.S25 and S26), it would be no difficult to assign the first two

absorptions to 8-HQ, and the third one to BPEB¹². Furthermore, the molar extinction coefficients of 5 at the wavelengths of 370 and 325 nm are 4.29×10^4 and 4.78×10^4 L mol⁻¹ cm⁻¹, respectively, and those for R1 at 320 and 240 nm are 1.85×10^3 and 1.98×10^4 L mol⁻¹ cm⁻¹, respectively. Fluorescence quantum yield measurements revealed the big difference between the two fluorophores, and the results are shown in Table S2. Further inspection of Fig.S1 reveals a clear inner filtering effect at concentrations higher than 4×10^{-5} mol L⁻¹.

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