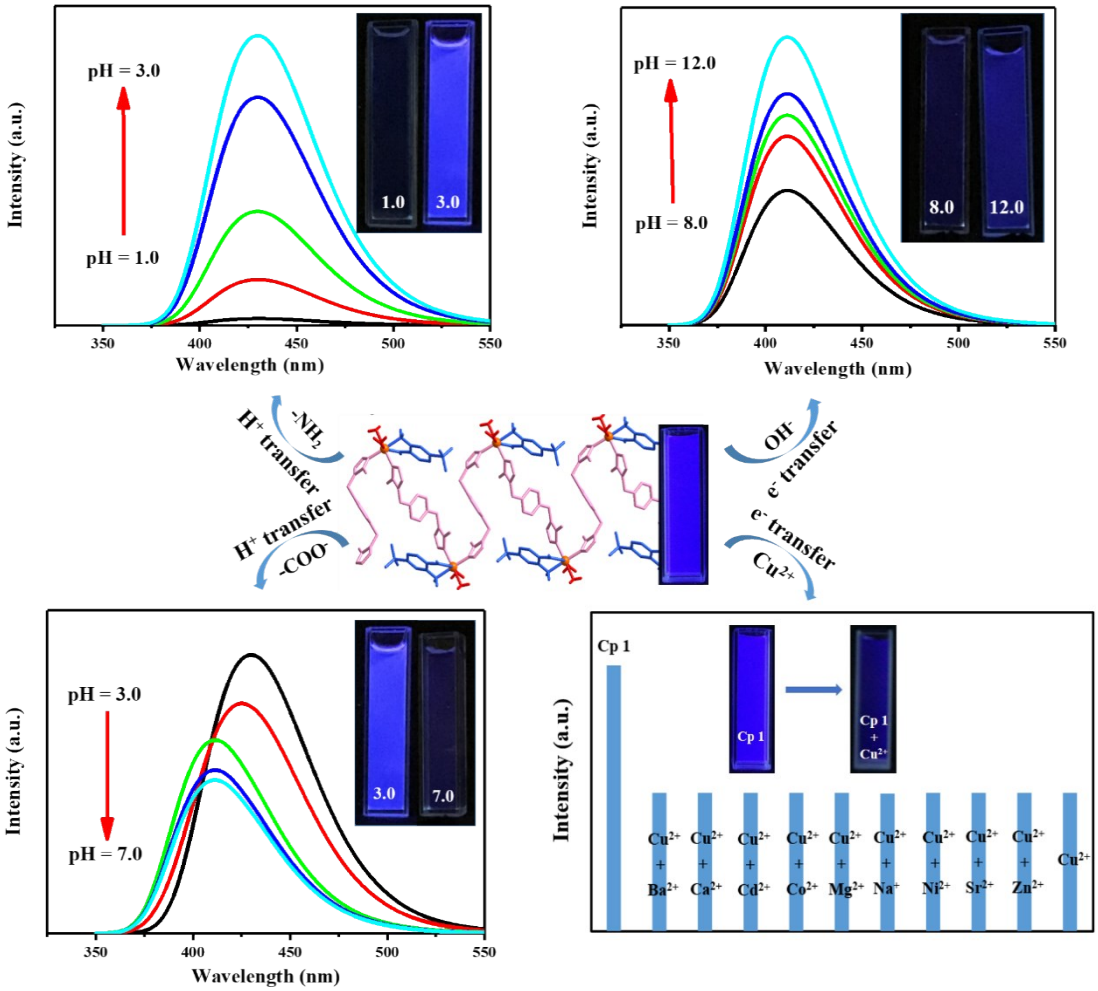
Single-crystal x-ray structure refinement

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on water were initially added through Fourier map and then refined with the restrianed parameters: O-H = 0.85(1) Å, H…H = 1.39(1) Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The other H atoms were added in calculated positions and were refined with C-H = 0.93 Å (aromatic), N-H = 0.86 Å (amino) with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms and $U_{iso}(H) = 1.2U_{eq}(N)$ for amino H atoms, respectively. Crystal data and structure refinement details are listed in **Table 1**.



Scheme S1 A novel CP-based fluorescent sensory material (**1**), showing distinct dual responsive fluorescence sensing to pH in three continuous stages as well as efficient and selective turn-off sensing to Cu^{2+}.

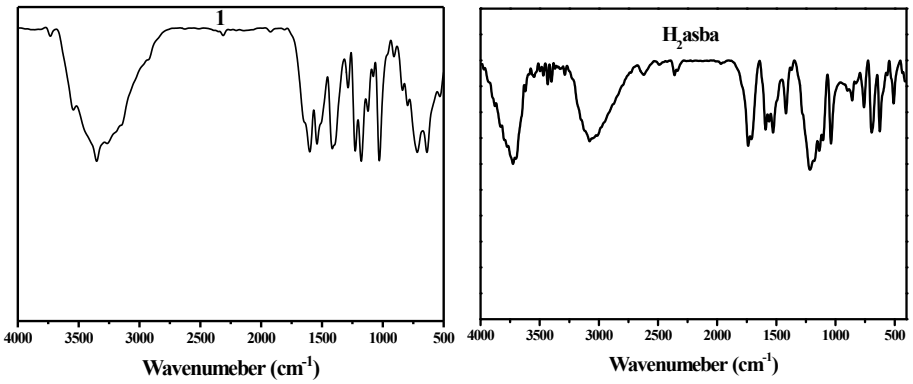


Figure S1 FT-IR spectrum of **1** and H_2asba.

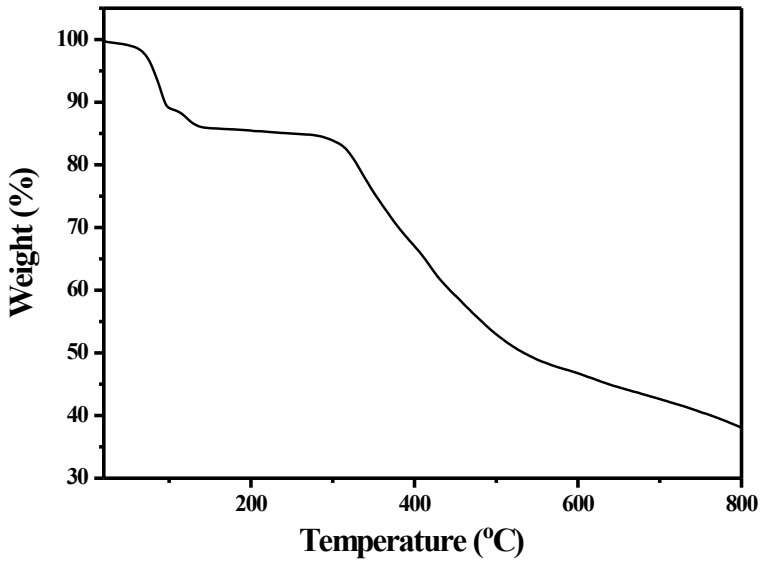


Figure S2 Thermogravimetric analysis (TGA) of **1**.

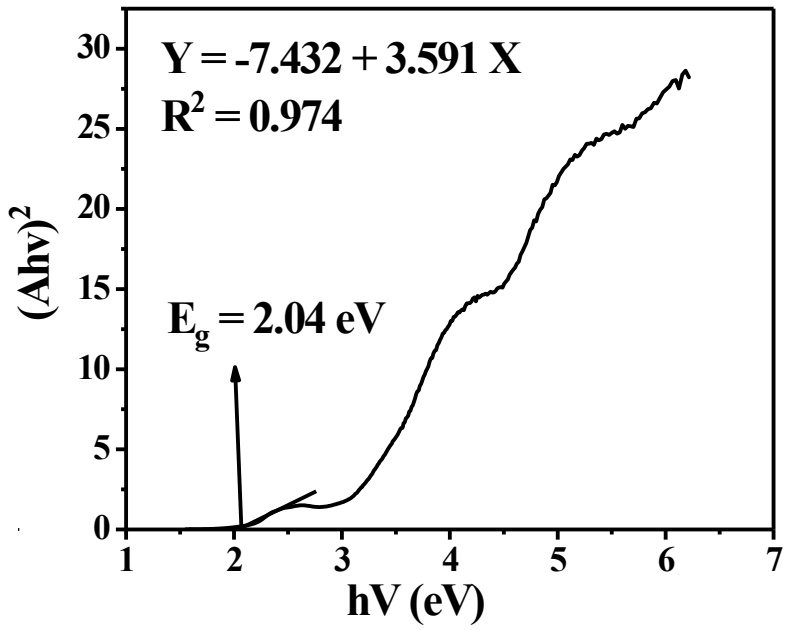


Figure S3 Solid-state diffuse reflectance UV-Vis-NIR spectrum of $(Ah\upsilon)^2$ against hυ (eV) for **1**.

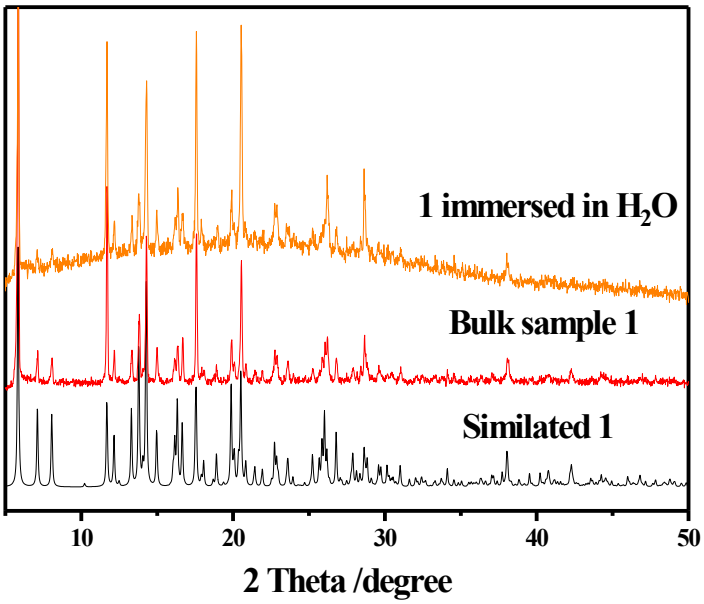


Figure S4 PXRD patterns of **1**: the simulated XRD pattern calculated using Mercury (black), the as-synthesized bulk sample of **1** (red), the sample after being soaked in water for about three days (orange).

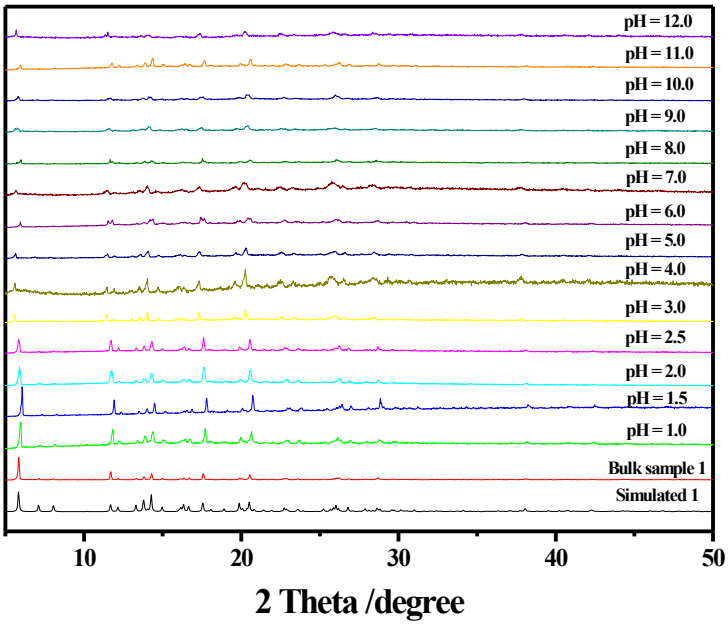


Figure S5 PXRD patterns of the bulk sample of **1** and those after being soaked in different pH (1-12) aqueous solutions.

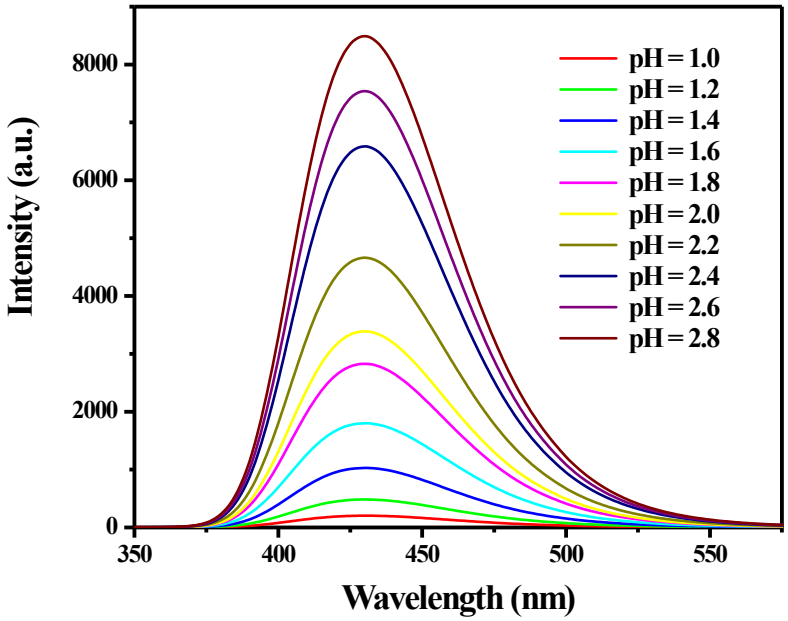


Figure S6 The fluorescence emission spectra of the well-ground sample **1** suspended in the artificial gastric juice with different pH values determined by the traditional pH meter**.**

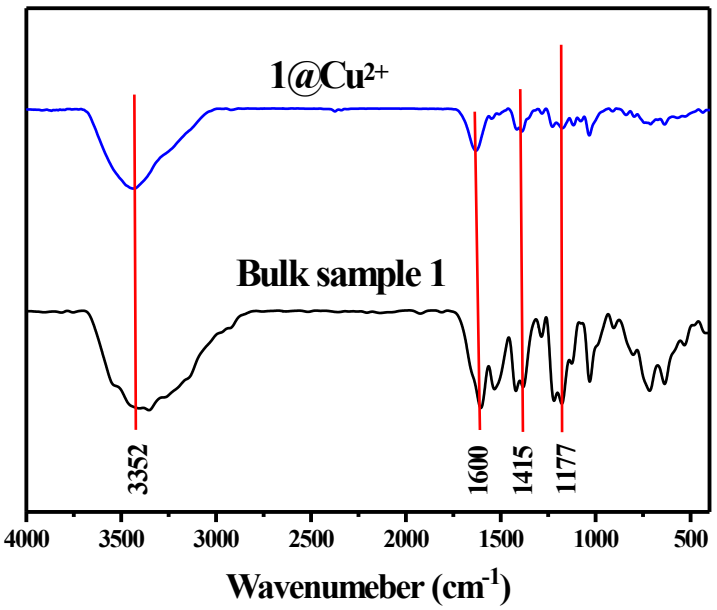


Figure S7 FT-IR spectra of **1**: the bulk sample of **1** (black), and that after being soaked in the aqueous Cu^{2+} solution for about three days (blue), respectively.

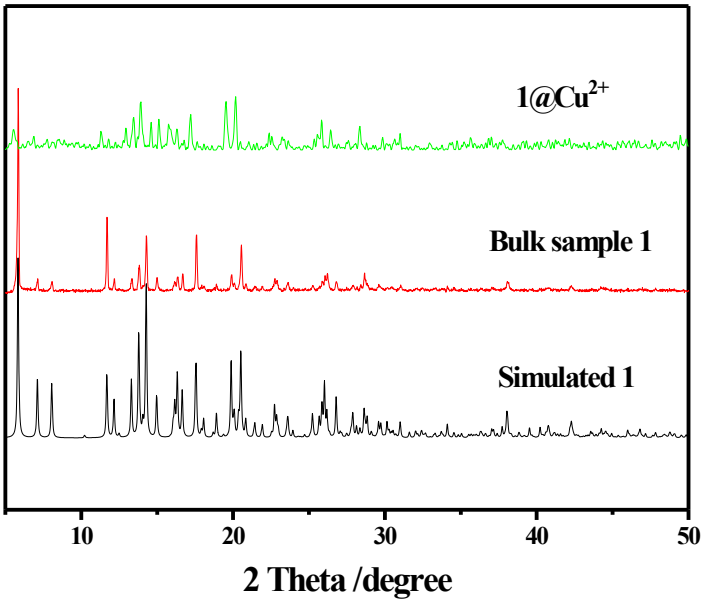


Figure S8 PXRD patterns of **1**: the simulated XRD pattern (black), the bulk sample of **1** (red), and that after being soaked in the aqueous Cu^{2+} solution (green), respectively.

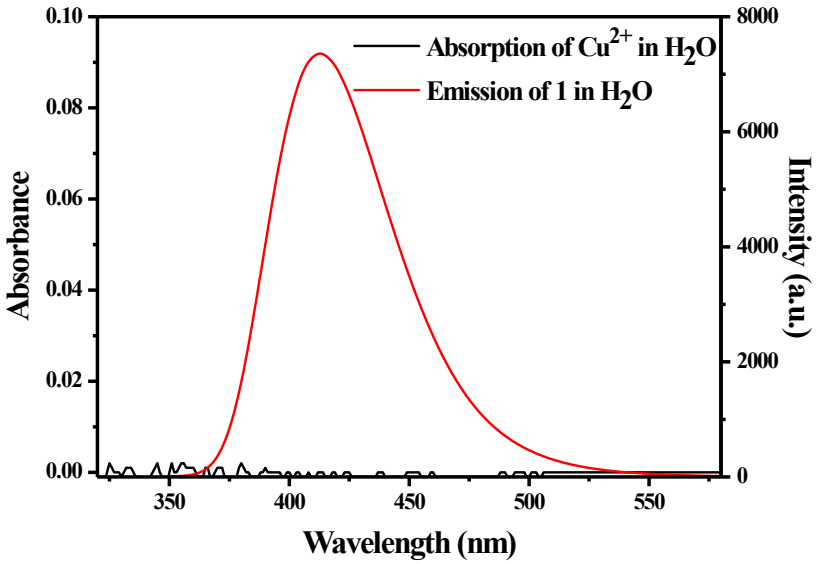


Figure S9 The spectral overlap between the absorption spectrum of Cu^{2+} (0.75 mM) in water (black) and the fluorescence emission spectrum of the aqueous suspension of **1** (red) (λ_{ex} = 330 nm).

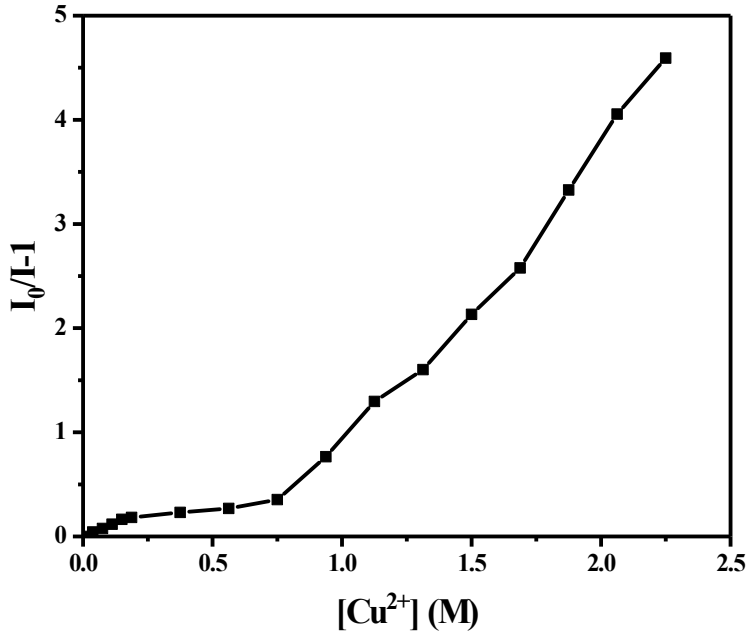


Figure S10 The linear plot of $I_0/I-1$ *v.s.* the concentration in the range of (0 - 2.25 mM).

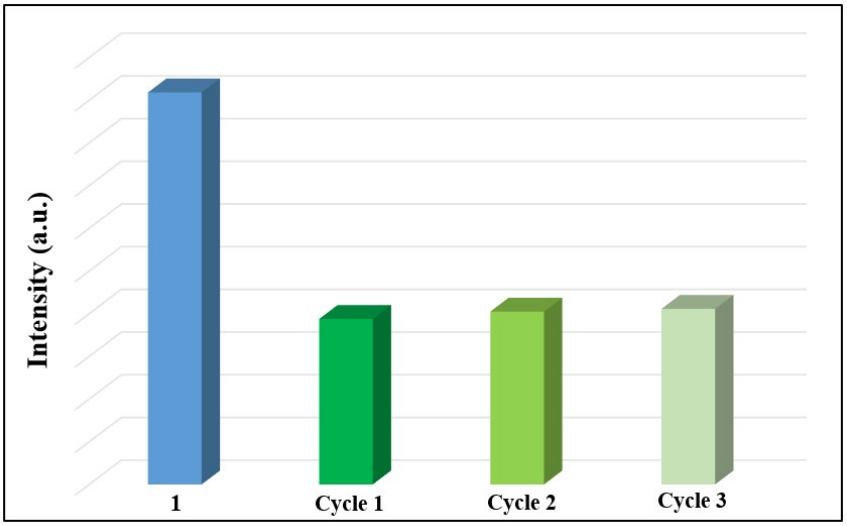


Figure S11 The fluorescence emission intensity of the aqueous suspensions of **1** before and after the addition of Cu^{2+} (0.75 mM) during three cycles**.**

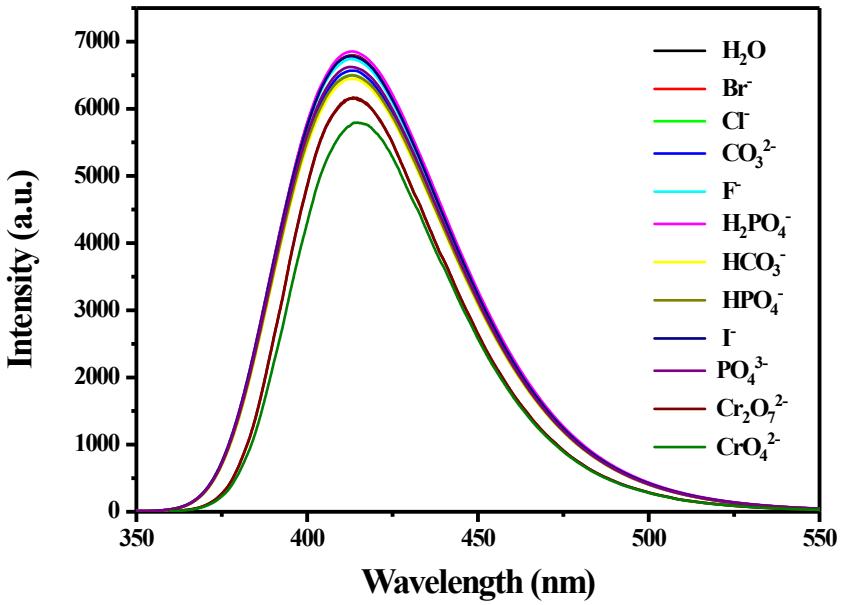


Figure S12 Effect of the inorganic anions (0.75 mM) on the fluorescence emission of the aqueous suspension of **1**.

Table S1 Selected geometric parameters (Å, º) for **1**.

Co1—N4	2.083 (3)	Co1—O4	2.090 (3)
Co1—N2	2.115 (4)	Co1—O5W	2.147 (3)
Co1—N1	2.199 (4)	Co1—O4W	2.082 (3)
O4W—Co1—N4	94.58 (11)	O4—Co1—O5W	85.18 (9)
O4W—Co1—O4	167.59 (9)	N2—Co1—O5W	176.82 (9)
N4—Co1—O4	93.52 (11)	O4W—Co1—N1	92.63 (10)
O4W—Co1—N2	91.80 (10)	N4—Co1—N1	171.33 (10)
N4—Co1—N2	93.36 (12)	O4—Co1—N1	78.60 (10)
O4—Co1—N2	97.10 (10)	N2—Co1—N1	91.22 (12)
O4W—Co1—O5W	85.62 (9)	O5W—Co1—N1	87.04 (11)
N4—Co1—O5W	88.71 (10)		

Table S2 Selected hydrogen-bond geometry (Å, º) for **1**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*W*—H3*WB*···O2^{i}	0.85	2.09	2.925 (5)	168
O5*W*—H5*WA*···O5^{ii}	0.87	2.02	2.739 (4)	139
O3*W*—H3*WA*···O1*W*^{ii}	0.85	2.01	2.778 (4)	149
N1—H1*A*···O5^{ii}	0.89	2.29	3.141 (5)	160
O4*W*—H4*WB*···O3*W*^{iii}	0.87	1.85	2.675 (4)	160
O4*W*—H4*WA*···O5^{iii}	0.87	1.96	2.797 (4)	163
N1—H1*B*···O5^{iii}	0.89	2.21	3.067 (5)	161

Symmetry codes: (i) *x*+1, *y*-1, *z*; (ii) -*x*+1, -*y*+1, -*z*; (iii) *x*-1, *y*, *z*.

Table S3 The relative fluorescence quantum yields of **1** in solvents.

solvent	Q_x
H_2O	0.1296
DMF	0.0675
THF	0.0017
AT	0.0597
MeOH	0.0111
CF	0.0014
EtOH	0.0048
AN	0.0047
IBA	0.0021