

**Luminescent Monomeric and Dimeric Ru(II) Acyclic
Carbene Complexes as Selective Sensors for NH₃/Amine
Vapor and Humidity**

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Electronic Supplementary Information

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1. Experimental Section

Materials and Reagents

Ruthenium(II) was obtained from Precious Metals Online. 2,2'-bipyridine (bpy) and 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy) were obtained from Meryer (Shanghai) Chemical Technology Company. Silver triflate (AgOTf) was obtained from Strem Chemicals Inc. 2-Aminopyridine (pyNH₂) was obtained from J&K Scientific Company. Solvents such as chloroform (Lab-Scan), dichloromethane (Lab-Scan), acetone (Lab-Scan), ethanol (Sigma-Aldrich), methanol (Lab-Scan) and *n*-hexane (Lab-Scan) were of analytical grade and used as received. Deuterated solvents for NMR spectroscopic measurements were obtained from Cambridge Isotope Laboratories, Inc. 4-Chlorophenyl isocyanide (4-ClC₆H₄NC) was prepared according to reported literature procedures. [Ru(bpy)₂Cl], [Ru(Me₂bpy)₂Cl] and [Ru(Me₂bpy)₂(CNR)(Cl)] (R = C₆H₄Cl-4) were prepared according to modified literature procedures.¹

Synthesis and characterization

{Ru(bpy)₂(N[^]C-Cl)⁺ OTf⁻} (**1**):

An ethanol solution (20 ml) of [Ru(bpy)₂(CNC₆H₄Cl-4)(Cl)] (100 mg, 175 μmol) and AgOTf (44.5 mg, 175 μmol) was refluxed for 2 hours. After cooling to room temperature, the precipitated AgCl was filtered. After that, 2-aminopyridine (19.8 mg, 210 μmol) was added into the filtrate. The mixture was warmed to 80 °C and stirred at this temperature for additional 4 hours. After cooling to room temperature, the solvent was removed by rotatory evaporation. The target product was isolated by column chromatography on alumina using dichloromethane-acetone (4:1, v/v) as eluent. The red precipitate was formed after washed by diethyl ether for two times. Further purification can be achieved by recrystallization from slow evaporation of acetone/hexane solution to give the analytically pure complex **1** as red solid. Yield: 33

mg, 41 μmol ; 23.4%. ^1H NMR (600 MHz, MeOD) δ 8.87 (1H, d, $J = 5.5$ Hz, 6-pyridyl H's of bpy), 8.58 (3H, m, three 6-pyridyl H's of bpy), 8.39 (1H, d, $J = 8.1$ Hz, 6-pyridyl H's of N[^]C-Cl), 8.09 (1H, t, $J = 7.9$ Hz, 5-pyridyl H's of bpy), 8.05 (1H, t, $J = 7.9$ Hz, 5-pyridyl H's of bpy), 8.01 (1H, t, $J = 6.6$ Hz, 5-pyridyl H's of bpy), 7.82 (1H, t, $J = 7.4$ Hz, 5-pyridyl H's of N[^]C-Cl), 7.80 (1H, d, $J = 5.6$ Hz, 3-pyridyl H's of bpy), 7.62 (1H, d, $J = 5.0$ Hz, 3-pyridyl H's of bpy), 7.54 (3H, m, 4-pyridyl H's of bpy, 5-pyridyl H's of bpy and 3-pyridyl H's of N[^]C-Cl), 7.49 (1H, t, $J = 7.2$ Hz, 4-pyridyl H's of bpy), 7.45 (1H, t, $J = 7.5$ Hz, 4-pyridyl H's of bpy), 7.27 (1H, d, $J = 8.2$ Hz, 3-pyridyl H's of bpy), 7.15 (1H, d, $J = 5.8$ Hz, 3-pyridyl H's of bpy), 7.11 (1H, t, $J = 6.3$ Hz, 4-pyridyl H's of N[^]C-Cl), 7.01 (4H, m, 2-,3-,5-,6- phenyl H's of N[^]C-Cl), 6.57 (1H, t, $J = 6.5$ Hz, 4-pyridyl H's of bpy). ^{13}C NMR (151 MHz, MeOD) δ 226.03, 206.52, 168.17, 157.26, 157.21, 156.77, 154.95, 154.59, 150.74, 150.17, 148.17, 147.49, 141.24, 137.34, 136.66, 136.07, 135.64, 134.85, 128.58, 128.11, 126.98, 126.76, 126.17, 124.60, 123.59, 123.24, 123.08, 123.03, 121.45, 119.34, 115.16, 113.24, 28.16. Positive-ion ESI-MS: m/z : 646.1 [M + H]⁺. IR (KBr disc): ν/cm^{-1} : 3463, 1620 (N–H), 1536, 1277 (C–N). Anal. Calcd for C₃₃H₂₅ClF₃N₇O₃RuS·(CH₄O) (825.2): C, 49.49; H, 3.54; N, 11.88. Found: C, 49.99; H, 3.266; N, 11.83.

{Ru(Me₂bpy)₂(N[^]C-Cl)⁺ OTf⁻} (2):

The complex was synthesized with a similar procedure for **1** except [Ru(Me₂bpy)₂(CNC₆H₄Cl-4)(Cl)] (66 mg, 100 μmol) was used instead of [Ru(bpy)₂(CNC₆H₄Cl-4)(Cl)]. Yield: 30 mg, 35.3 μmol ; 35.3%. ^1H NMR (600 MHz, MeOD) δ 8.63 (1H, d, $J = 6.0$ Hz, 6-pyridyl H's of Me₂bpy), 8.45 (3H, m, three 3-pyridyl H's of Me₂bpy), 8.23 (1H, s, 3-pyridyl H's of Me₂bpy), 7.60 (1H, t, $J = 7.9$ Hz, 4-pyridyl H's of N[^]C-Cl), 7.58 (1H, d, $J = 5.7$ Hz, 6-pyridyl H's of Me₂bpy), 7.40 (2H, m, 5-pyridyl H's of Me₂bpy and 6-pyridyl H's of Me₂bpy), 7.34 (1H, d, $J = 6.6$ Hz, 5-pyridyl H's of Me₂bpy), 7.32 (1H, d, $J = 8.3$ Hz, 3-pyridyl H's of N[^]C-Cl), 7.29 (1H, d, $J = 4.8$ Hz, 5-pyridyl H's of Me₂bpy), 7.23 (1H, d, $J = 5.3$ Hz, 6-pyridyl H's of

Me₂bpy), 7.20 (1H, d, *J* = 6.0 Hz, 6-pyridyl H's of N⁺C-Cl), 7.05 (1H, d, *J* = 2.3 Hz, 3-phenyl H's of N⁺C-Cl), 7.04 (1H, d, *J* = 3.7 Hz, 5-phenyl H's of N⁺C-Cl), 6.90 (3H, m, 2-,6-phenyl H's of N⁺C-Cl and 5-pyridyl H's of Me₂bpy), 6.66 (1H, t, *J* = 6.6 Hz, 5-pyridyl H's of N⁺C-Cl), 2.62 (3H, s, three CH₃ H's of Me₂bpy), 2.58 (3H, s, three CH₃ H's of Me₂bpy), 2.53 (3H, s, three CH₃ H's of Me₂bpy), 2.45 (3H, s, three CH₃ H's of Me₂bpy). ¹³C NMR (151 MHz, MeOD) δ 219.23, 207.22, 190.32, 167.93, 156.89, 156.74, 156.16, 154.78, 154.61, 154.55, 153.65, 153.62, 152.08, 150.24, 150.09, 149.51, 149.01, 148.71, 147.85, 147.78, 147.38, 142.88, 136.86, 136.42, 128.42, 127.79, 127.21, 127.09, 125.78, 124.40, 124.01, 123.80, 123.69, 19.82, 19.79, 19.70, 19.65. Positive-ion ESI-MS: *m/z*: 702.4 [M + H]⁺. IR (KBr disc): ν/cm⁻¹: 3443, 1617 (N-H), 1542, 1264 (C-N). Anal. Calcd for C₃₇H₃₃ClF₃N₇O₃RuS·2(C₄H₈O₂) (938.4): C, 52.48; H, 4.51; N, 10.45. Found: C, 52.19; H, 4.19; N, 10.23.

***{Ru(bpy)₂(CF₃-N⁺C-Cl)⁺ OTf⁻}* (3):**

The complex was synthesized with a similar procedure for **1** except 2-amino-3-(trifluoromethyl)pyridine (33.7 mg, 206 μmol) was used instead of 2-aminopyridine. Yield: 87 mg, 101 μmol; 49%. ¹H NMR (600 MHz, MeOD) δ 8.66 (1H, d, *J* = 4.7 Hz, 6-pyridyl H's of bpy), 8.62 (1H, d, *J* = 8.2 Hz, 6-pyridyl H's of bpy), 8.58 (2H, d, *J* = 8.2 Hz, two 6-pyridyl H's of bpy), 8.51 (1H, d, *J* = 7.2 Hz, 3-pyridyl H's of bpy), 8.07 (2H, m, two 5-pyridyl H's of bpy), 8.00 (1H, t, *J* = 7.2 Hz, 5-pyridyl H's of bpy), 7.94 (1H, t, *J* = 7.3 Hz, 4-pyridyl H's of bpy), 7.81 (1H, d, *J* = 7.4 Hz, 6-pyridyl H's of CF₃-N⁺C-Cl), 7.78 (2H, d, *J* = 5.6 Hz, 3-pyridyl H's of bpy), 7.65 (2H, d, *J* = 5.1 Hz, 3,5-phenyl H's of CF₃-N⁺C-Cl), 7.49 (3H, m, three 4-pyridyl H's of bpy), 7.40 (2H, m, 4-phenyl H's of CF₃-N⁺C-Cl and 3-pyridyl H's of bpy), 7.30 (1H, m, 5-pyridyl H's of bpy), 7.12 (2H, d, *J* = 6.9 Hz, 2,6-phenyl H's of CF₃-N⁺C-Cl), 6.60 (1H, t, *J* = 6.4 Hz, 5-phenyl H's of CF₃-N⁺C-Cl). ¹³C NMR (151 MHz, MeOD) δ 232.20, 210.05, 157.12, 156.96, 156.92, 154.82, 154.74, 151.17, 150.90, 150.02, 148.21, 139.28, 137.41, 136.13, 135.68, 135.44, 134.07, 127.71, 127.05, 126.84, 126.51, 126.38, 123.58,

123.28, 123.26, 123.14, 121.44, 119.33, 112.95, 69.19, 65.50, 54.65, 30.69, 28.13. ^{19}F NMR (565 MHz, MeOD) δ -65.25 (3F, s, CF_3 's of $\text{CF}_3\text{-N}^+\text{C-Cl}$). Positive-ion ESI-MS: m/z : 713.2 $[\text{M} + \text{H}]^+$. IR (KBr disc): ν/cm^{-1} : 3447, 1617 (N-H), 1534, 1259 (C-N). Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{ClF}_6\text{N}_7\text{O}_3\text{RuS}\cdot(\text{C}_6\text{H}_{14})$ (947.4): C, 47.42; H, 2.81; N, 11.39. Found: C, 47.53; H, 3.00; N, 10.87.

Physical measurements and instrumentation

^1H and ^{13}C spectra were recorded on a Bruker AVANCE III HD Ascend 600 MHz FT-NMR spectrometer. Chemical shifts (δ , ppm) were reported relative to tetramethylsilane (Me_4Si). IR spectra were obtained from KBr discs by using a Perkin-Elmer Spectrum 100 FTIR spectrophotometer. All ESI mass spectra were recorded on a PE-SCIEX API 365 EX single quadrupole mass spectrometer. Elemental analyses of all compounds were performed on an Elementar Vario MICRO Cube elemental analyzer. Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission at room temperature and at 77 K were recorded on Edinburgh Instruments FLS980 fluorescence spectrometer. Time-resolved emission and emission lifetime measurements were recorded on LP920 laser flash photolysis system using the third harmonic output (355 nm, 6-8 ns fwhm pulse width) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd:YAG laser as the excitation source. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze pump-thaw cycles. Measurements of the dichloromethane glass samples at 77 K were carried out with dilute dichloromethane sample solutions contained in a quartz tube inside a liquid nitrogen-filled quartz optical Dewar flask. The luminescence quantum yields of the solution emission were determined by using the optical-dilution method using aerated aqueous solution of $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$ ($\phi_{em} = 0.040$ with excitation at 436 nm) as reference

standard.² Luminescent quantum yields for solid state sample were determined using the integrating sphere assembly accessory (F-M01) of Edinburgh Instruments FLS980.

X-ray Crystal Structure Determination. The crystal structures were determined on a Xcalibur, Sapphire3, Gemini Ultra diffractometer using graphite monochromatized Cu-K α ($\lambda = 1.54178 \text{ \AA}$) or Mo-K α ($\lambda = 0.7107 \text{ \AA}$) radiation. The structures were solved by direct methods employing SHELXL-97 program³ on PC. Ir and many non-H atoms were located according to direct methods. The positions of other non-H atoms were found after successful refinement by full-matrix least-squares using SHELXL-97 program³ on PC. All non-H atoms were refined anisotropically in the final stage of least-squares refinement. The positions of hydrogen atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated carbon atoms, and participated in the calculation of final *R*-indices.

2. Data for single-crystal X-ray crystallography

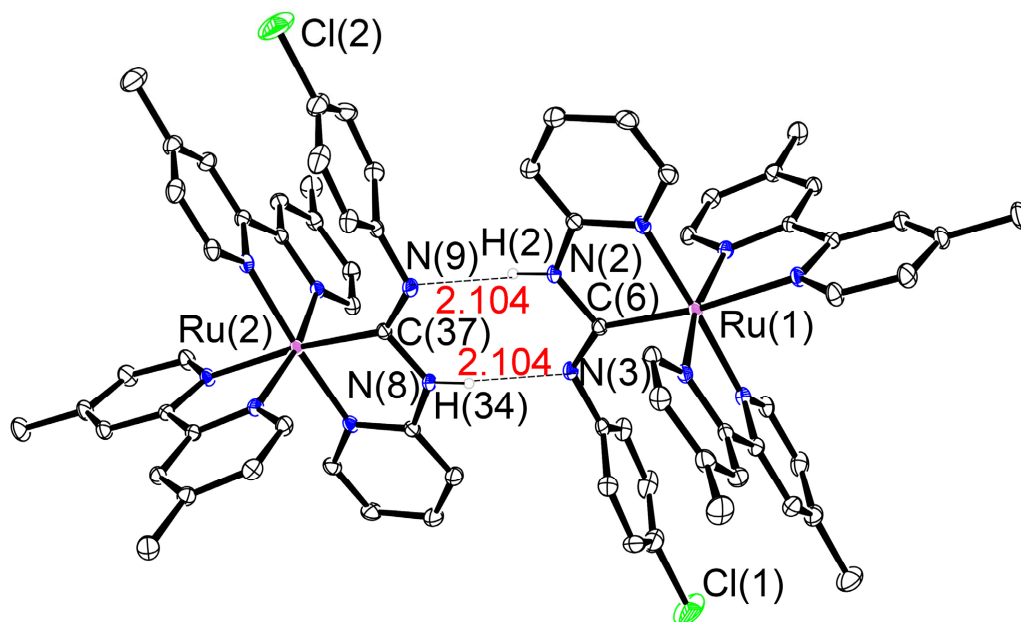


Fig. S1 Perspective drawing of H-bonded dimer of **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Table S1. Crystal and structure determination data for **1**, **2** and **3**.

	1	2	3
Formula	C ₃₃ H ₂₅ ClF ₃ N ₇ O ₃ RuS	C ₃₇ H ₃₃ ClF ₃ N ₇ O ₃ RuS	C ₃₄ H ₂₄ ClF ₆ N ₇ O ₃ RuS·(C ₆ H ₁₄)
Molecular weight	793.18	849.28	947.35
<i>T</i> / K	173	193	213
<i>a</i> / Å	20.2684(4)	10.8630 (5)	9.1118 (2)
<i>b</i> / Å	9.7474 (2)	11.2065 (5)	45.0472
<i>c</i> / Å	32.7825 (7)	16.9747 (8)	10.0818 (3)
α / deg	90	84.7950(10)	90
β / deg	91.016 (1)	85.957 (2)	93.4150(10)
γ / deg	90	63.490 (1)	90
<i>V</i> / Å ³	6475.6 (2)	1840.49 (15)	4130.84 (19)
Crystal color	Yellow	Red	Red
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> <i>c</i>
<i>Z</i>	8	2	4
<i>F</i> (000)	3200	864	1928
<i>D</i> _{<i>c</i>} / gcm ⁻³	1.627	1.532	1.523
Crystal dimensions / mm	0.49 × 0.21 × 0.02	0.45 × 0.31 × 0.02	0.41 × 0.25 × 0.01
λ / Å	1.54178	0.71073	1.54178
μ / mm ⁻¹	5.85	0.62	4.79
Collection range	2.2 ≤ θ ≤ 74.6° (<i>h</i> : -25 to 25; <i>k</i> : -12 to 12; <i>l</i> : -35 to 40)	2.38 ≤ θ ≤ 26.33° (<i>h</i> : -13 to 13; <i>k</i> : -14 to 13; <i>l</i> : -21 to 20)	3.9 ≤ θ ≤ 72.4° (<i>h</i> : -11 to 11; <i>k</i> : -55 to 55; <i>l</i> : -12 to 12)
Completeness to theta	99.9%	99.5%	99.4%
No. of data collected	76374	20290	41339
No. of unique data	13206	7501	7431
No. of data used in refinement, <i>m</i>	10488	6084	7431
No. of parameters refined, <i>p</i>	883	482	535
<i>R</i> ^a	0.034	0.046	0.024
<i>wR</i> ^a	0.085	0.114	0.0572
Goodness-of-fit, <i>S</i>	1.03	1.03	1.01
Maximum shift, (Δ/σ) _{max}	0.003	0.002	0.005
Residual extrema in final difference map, eÅ ⁻³	+0.71, -0.67	+0.90, -0.91	+0.38, -0.25

$$^a w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bP], \text{ where } P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$$

Table S2. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1**.

Ru(1)–N(6)	2.068 (2)	Ru(1)–N(7)	2.056 (2)
Ru(1)–N(4)	2.140 (2)	Ru(1)–N(5)	2.072 (2)
Ru(1)–N(1)	2.071 (2)	Ru(1)–C(6)	2.042 (2)
C(6)–N(3)	1.297 (4)	C(6)–N(2)	1.408 (3)
<hr/>			
C(6)–Ru(1)–N(1)	79.79 (9)	N(4)–Ru(1)–N(5)	77.56 (9)
N(6)–Ru(1)–N(7)	78.45 (9)	N(6)–Ru(1)–N(1)	176.61 (9)
N(7)–Ru(1)–N(5)	169.33 (8)	N(4)–Ru(1)–C(6)	168.44 (10)
Ru(1)–C(6)–N(3)	137.67 (19)	Ru(1)–C(6)–N(2)	110.60 (17)
N(3)–C(6)–N(2)	111.5 (2)		

Table S3. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **2**.

Ru(1)–N(6)	2.053 (3)	Ru(1)–N(7)	2.047 (3)
Ru(1)–N(4)	2.064 (3)	Ru(1)–N(5)	2.141 (3)
Ru(1)–N(1)	2.063 (3)	Ru(1)–C(6)	2.032 (3)
C(6)–N(3)	1.301 (4)	C(6)–N(2)	1.406 (4)
<hr/>			
C(6)–Ru(1)–N(1)	79.91 (12)	N(4)–Ru(1)–N(5)	77.48 (11)
N(6)–Ru(1)–N(7)	78.77 (12)	N(6)–Ru(1)–N(1)	174.06 (11)
N(7)–Ru(1)–N(4)	168.35 (10)	N(5)–Ru(1)–C(6)	171.82 (12)
Ru(1)–C(6)–N(3)	138.0 (3)	Ru(1)–C(6)–N(2)	110.8 (2)
N(3)–C(6)–N(2)	111.2 (3)		

Table S4. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **3**.

Ru(1)–N(6)	2.068 (3)	Ru(1)–N(7)	2.151 (2)
Ru(1)–N(4)	2.067 (3)	Ru(1)–N(5)	2.054 (3)
Ru(1)–N(1)	2.066 (3)	Ru(1)–C(6)	2.014 (3)
C(6)–N(3)	1.366 (4)	C(6)–N(2)	1.328 (4)
<hr/>			
C(6)–Ru(1)–N(1)	76.88 (11)	N(4)–Ru(1)–N(5)	79.07 (11)
N(6)–Ru(1)–N(7)	77.22 (10)	N(4)–Ru(1)–N(1)	172.10 (10)
N(7)–Ru(1)–C(6)	171.92 (12)	N(5)–Ru(1)–N(6)	170.05 (10)
Ru(1)–C(6)–N(3)	124.9 (2)	Ru(1)–C(6)–N(2)	118.5 (2)
N(3)–C(6)–N(2)	116.6 (3)		

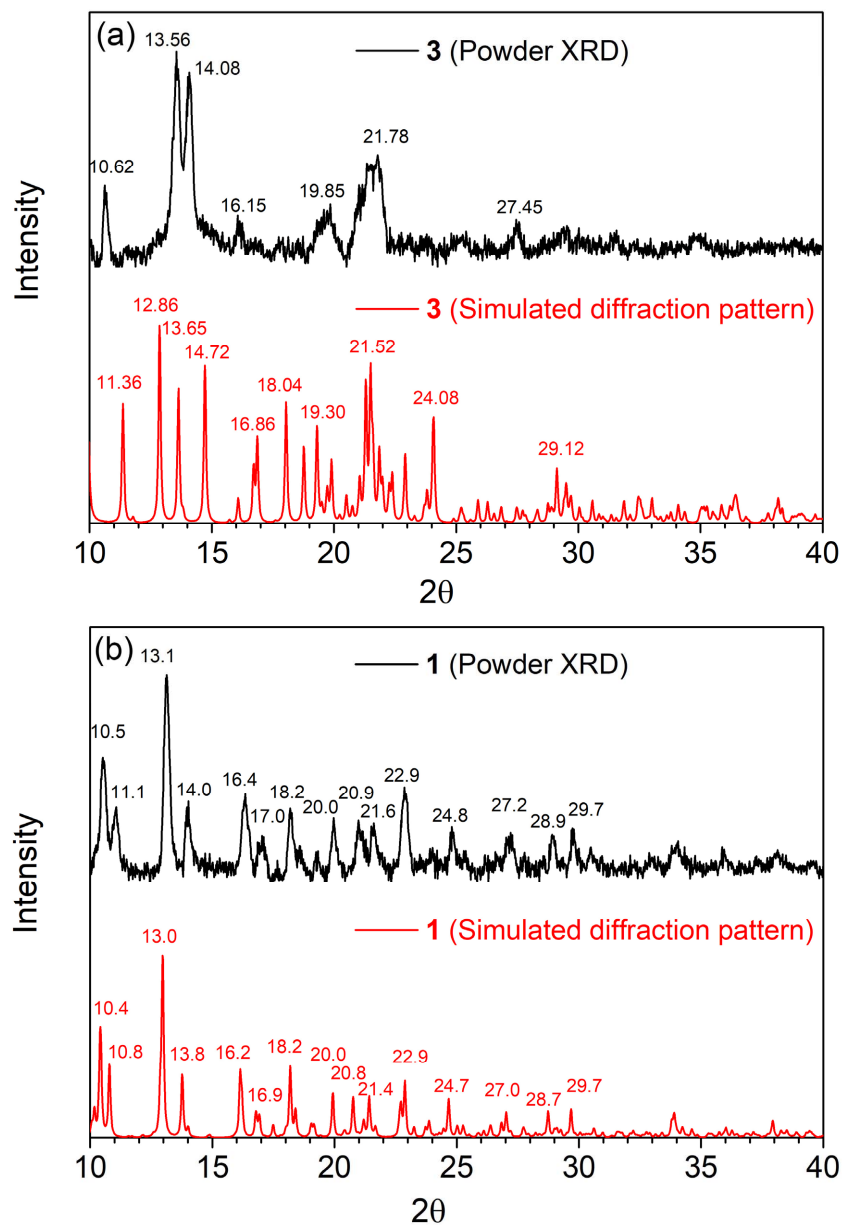


Fig. S2 Powder XRD pattern (black line) and simulated diffraction pattern (red line) from the single crystal data of (a) **3** and (b) **1**.

3. Photophysical properties and dimerization equilibrium analysis in dichloromethane solution

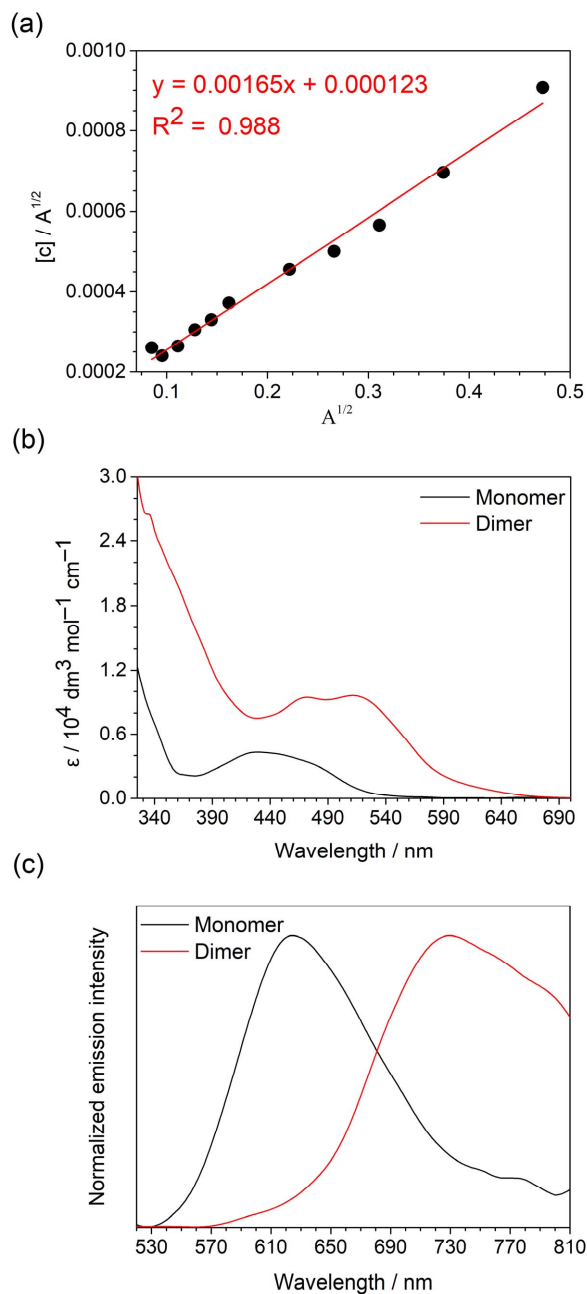


Fig. S3 (a) A linear fit in the plot of $[2]/A^{1/2}$ vs. $A^{1/2}$ at 615 nm in the absorption spectrum of **2** in dichloromethane solution. (b) Calculated absorption spectra of the dimeric and monomeric forms of **2** in dichloromethane solution based on the dimerization equilibrium analysis. (c) Time-resolved emission spectra of **2**.

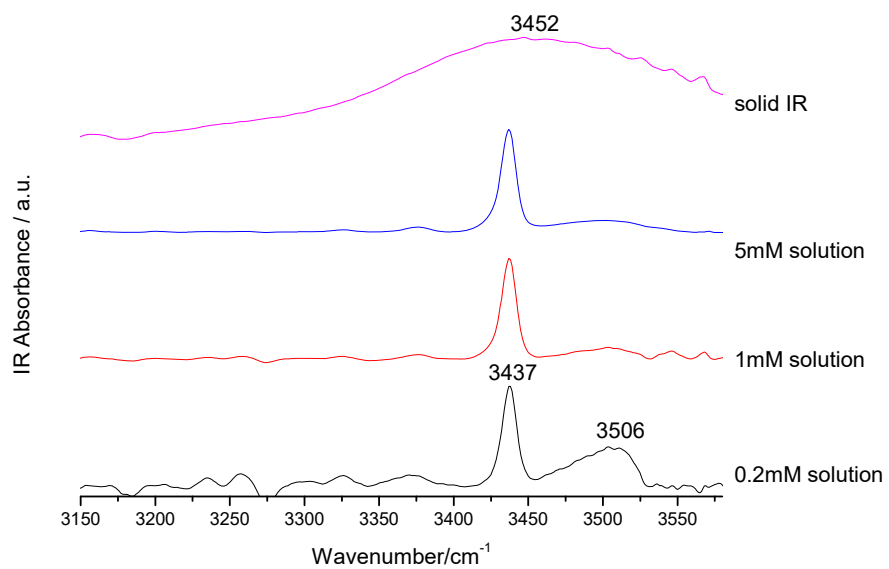


Fig. S4. IR spectra of solid state and dichloromethane solutions of **1** at different concentrations (5mM, 1mM and 0.2mM).

Dimerization equilibrium analysis

$2M \rightleftharpoons D$ where M, D are the monomer and dimer, respectively.

$$K = \frac{[D]}{[M]^2}$$

$$[M] = \pm \sqrt{[D]/K} \quad -\sqrt{[D]/K} \text{ is rejected as } [M] \text{ is a non-negative value}$$

$$[C] = [M] + 2[D]$$

$$[C] = \sqrt{[D]/K} + 2[D]$$

$$[C] = \sqrt{A/K\epsilon_D} + \frac{2A}{\epsilon_D}$$

$$\frac{[C]}{\sqrt{A}} = \frac{1}{\sqrt{K\epsilon_D}} + \frac{2}{\epsilon_D} \sqrt{A}$$

Where [M] and [D] are the concentration of the monomer and dimer, [C] is the total concentration of all complexes, ϵ_D is the extinction coefficient of dimeric form and A is the absorbance at which only the dimer form absorb, K is the equilibrium constant of the dimerization.

From the above equation, a linear relationship between $[C]/(A)^{1/2}$ and $(A)^{1/2}$ should be established for the equilibrium of the dimerization process.

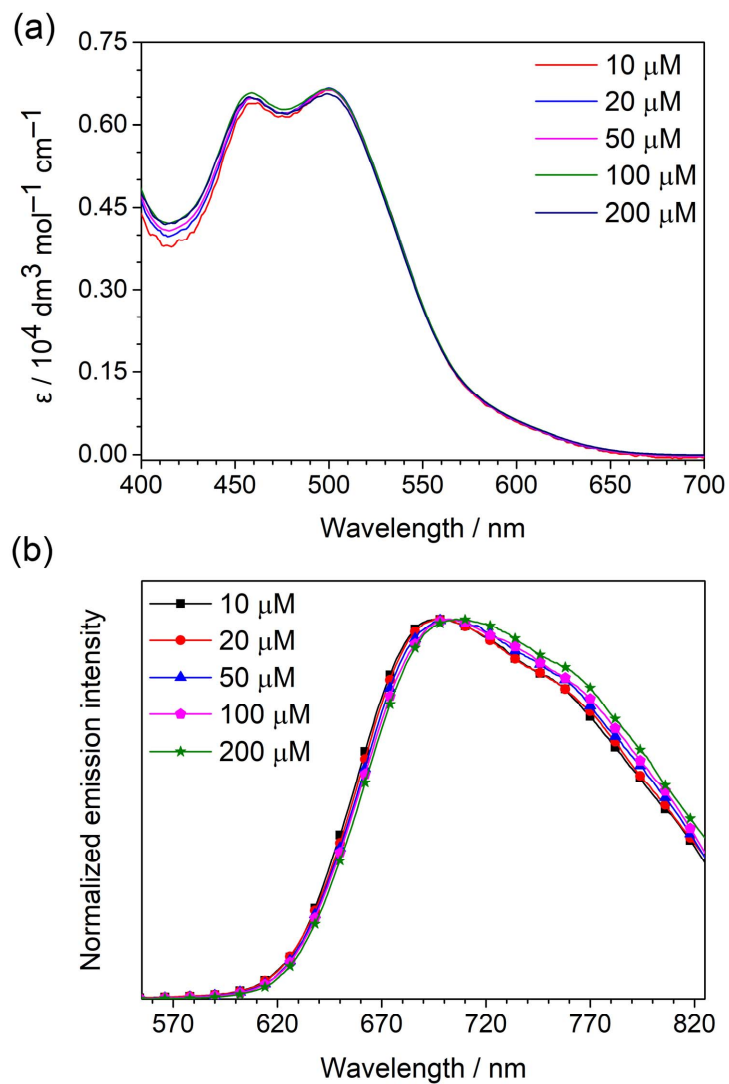


Fig. S5 (a) Overlaid UV-vis absorption and (b) emission spectra of different concentrations of **3** in dichloromethane solution. Excitation wavelength: 436 nm.

Table S5. Photophysical properties of **1 – 3** (concentration = 25 μM).

	Medium	Emission (Monomer) $\lambda_{\text{em}} / \text{nm}$ ($\tau_0 / \mu\text{s}$)	Emission (Dimer) $\lambda_{\text{em}} / \text{nm}$ ($\tau_0 / \mu\text{s}$)	$\phi_{\text{em (Monomer)}} / \%$, $\phi_{\text{em (Dimer)}} / \%$	Absorption ^a $\lambda_{\text{abs}} / \text{nm}$ (Monomer) ($\epsilon / 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	Absorption ^a $\lambda_{\text{abs}} / \text{nm}$ (Dimer) ($\epsilon / 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
1	CH_2Cl_2^a	627 (0.26)	721 (0.088)	0.13, 0.05	423 (0.44), sh 446 (0.43)	467 (1.03), 514 (1.11)
	Glass ^b	599, 685 sh (4.46)	668, 715 sh (0.97)			
	Glass ^c	584, 625 sh (4.33)	- ^d			
2	CH_2Cl_2^a	623 (0.19)	729 (0.081)	0.14, 0.15	428 (0.43), sh 473 (0.34)	470 (0.94), 515 (0.96)
	Glass ^b	586, 623 sh (4.41)	676 (0.72), 734 sh			
	Glass ^c	587, 626 sh (3.89)	- ^d			
3	CH_2Cl_2^a	- ^d	698 (0.16), 754 sh	- ^d , 0.28	\	458 (0.65), 500 (0.66)
	Glass ^b	- ^d	654 (1.04), 707 sh			
	Glass ^c	562, 600 sh (5.86)	651 (0.99), 705 sh			

^aIn CH_2Cl_2 solution at 298 K. ^b CH_2Cl_2 glass at 77 K. ^cEtOH/MeOH (v/v 4:1) glass at 77 K. ^dToo low to be accurately determined.

4. Solvatochromic behavior of **1**

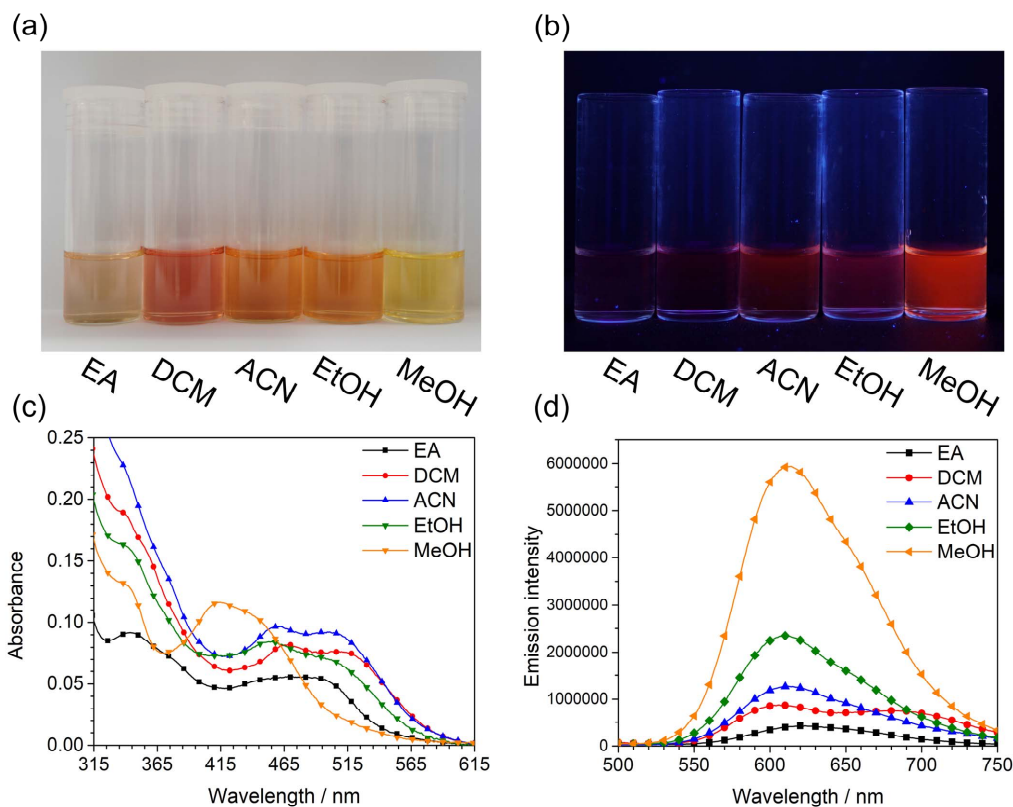


Fig. S6 Photos of the solution captured under (a) daylight and (b) UV illumination under a dark condition are shown in the upper panel. (c) Overlaid UV-vis absorption and (d) emission spectra of **1** in different solvents at 298 K. Concentration: 23 μ M.

Table S6. Emission data of **1** in different solvents at 298 K.

Solvent Medium	λ_{em} / nm	Emission (τ_0 / ns)
Ethylacetate	622	264, 39
Dichloromethane	606, 691	260, 90
Acetonitrile	612	405, 40
Ethanol	610	340, 49
Methanol	613	363

5. Selected emission spectra of 1 – 3

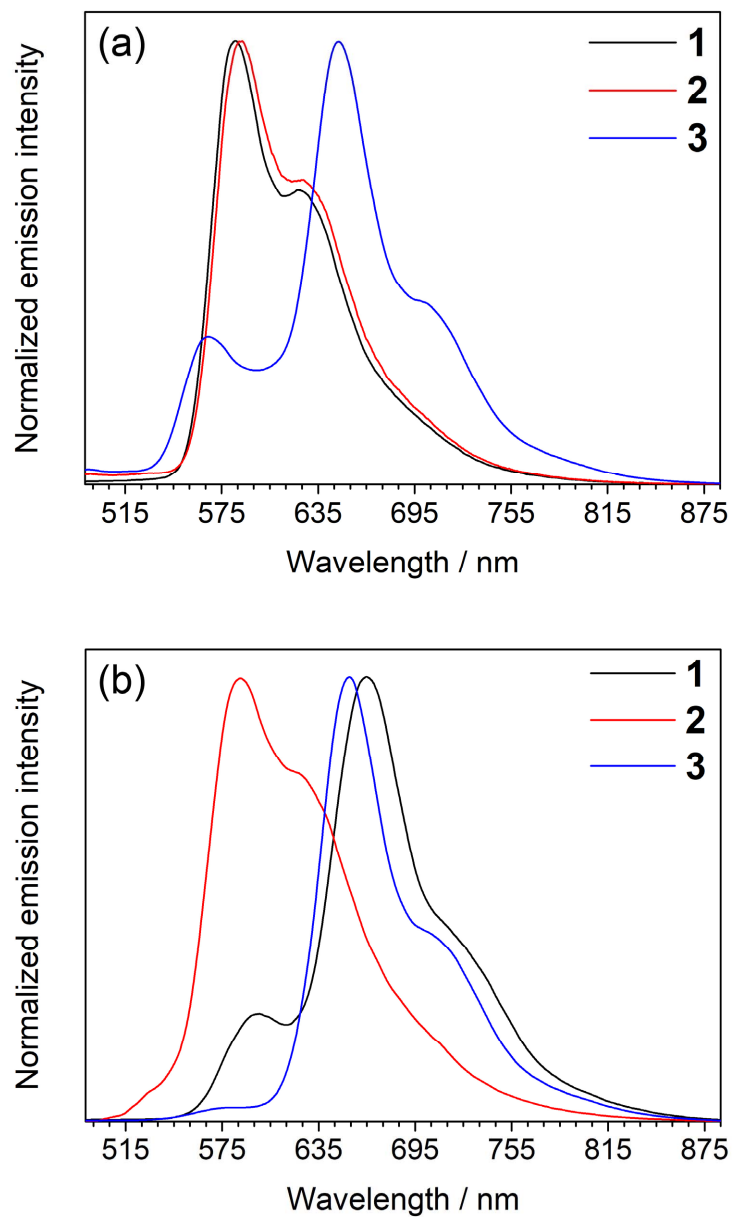


Fig. S7 Overlaid emission spectra of 1 – 3 in (a) EtOH/MeOH (v/v 4:1) glass and CH₂Cl₂ solid at 77 K Concentration: 25 μ M.

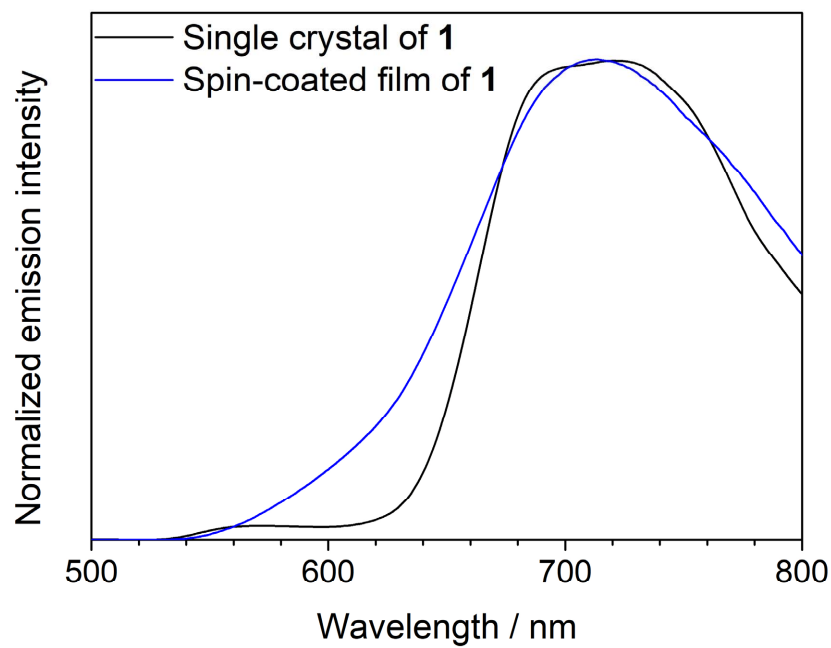


Fig. S8 Overlaid emission spectra the single crystal sample and spin-coated thin film of **1**.

6. Emission responses of 1M_s towards amine vapors

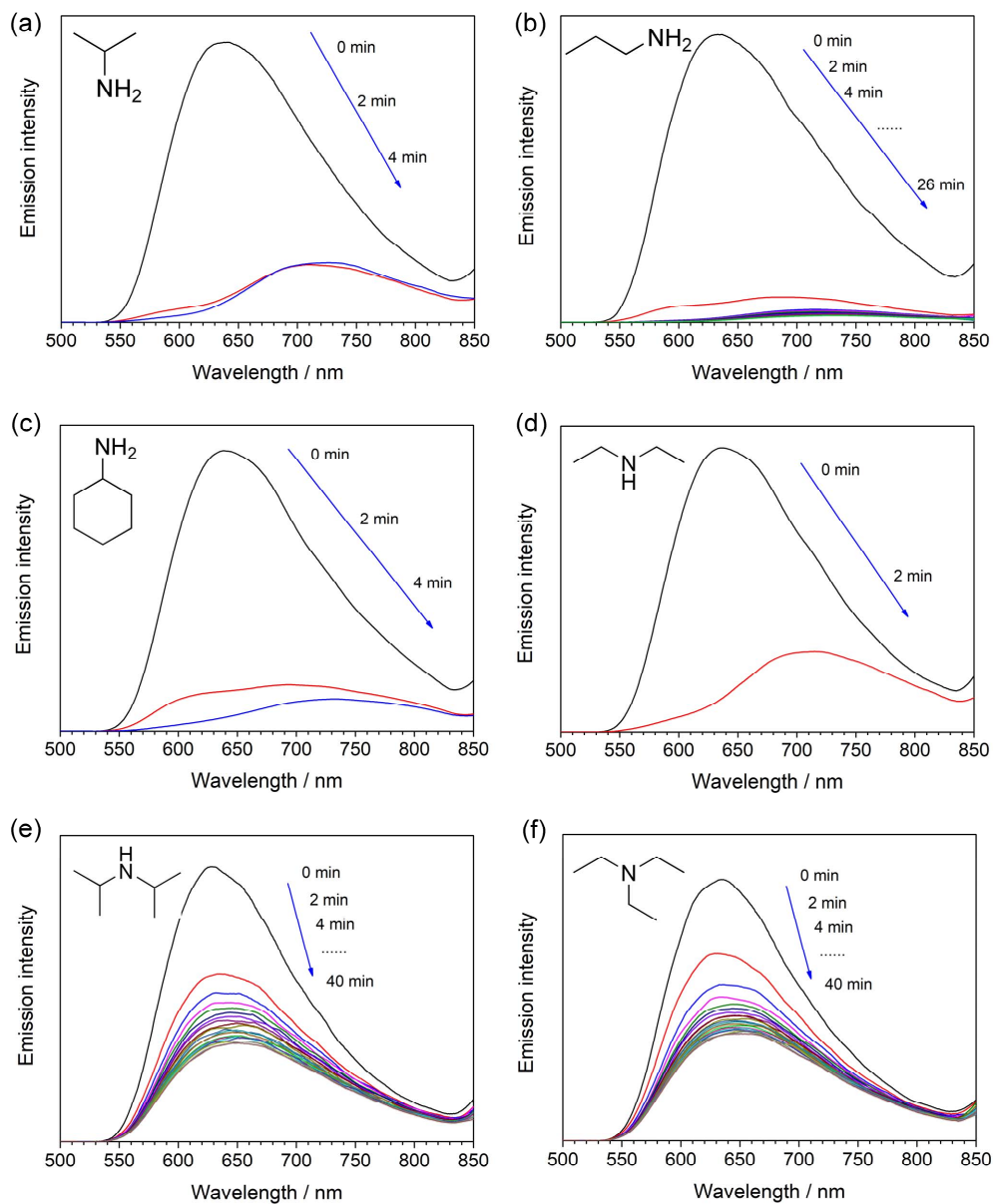


Fig. S9 Emission spectral changes of the thin films of **1** (**1M_s**) upon exposure to different types of saturated amines vapor.

7. UV-vis absorption and NMR study of the interaction of **1** with isopropylamine

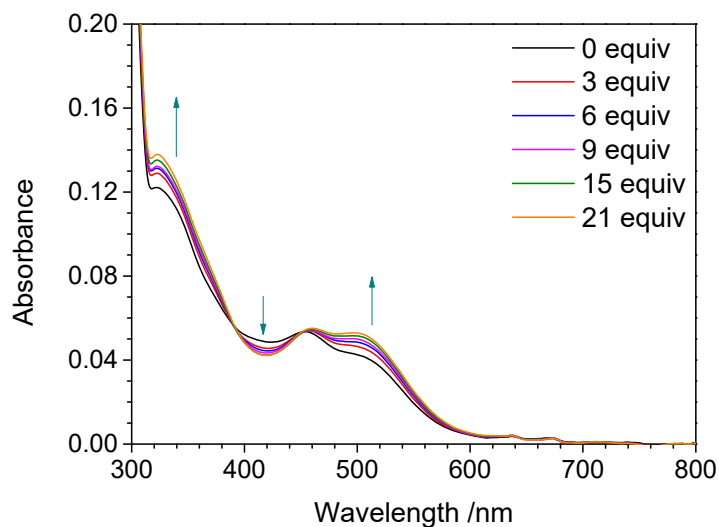


Fig. S10 UV-vis absorption spectral changes of **1** in MeCN solution (2 μM) in 5-cm cuvette upon addition of different mole equivalents (3, 6, 9, 15 and 21) of isopropyl amine.

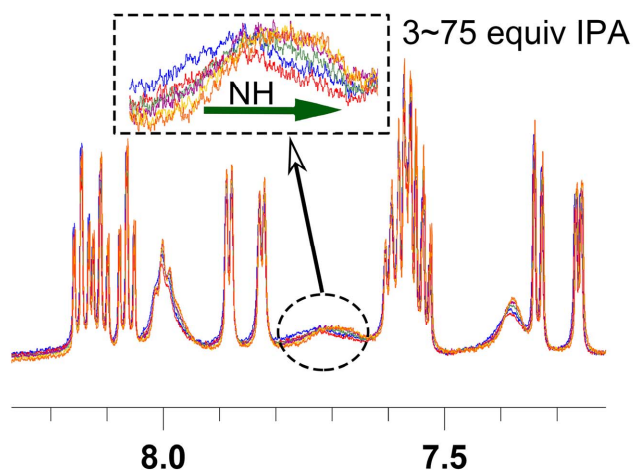


Fig. S11 ¹H NMR spectral changes of **1** upon addition of different mole equivalents (0, 3, 12, 30, 45, 75) of isopropylamine (IPA) in acetone-*d*₆.

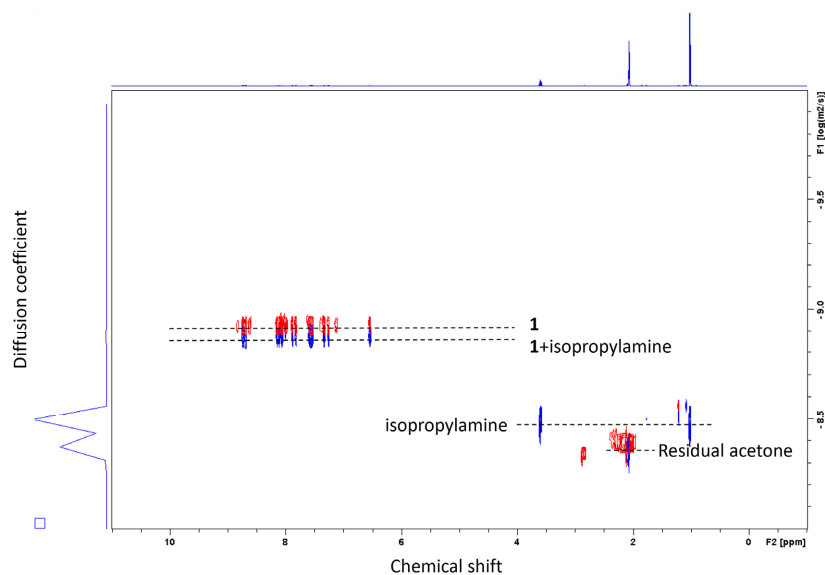


Fig. S12 DOSY spectrum of 0.5 mM of **1** in acetone- d_6 at 25 °C before and after the addition of 75 mole equivalent of IPA.

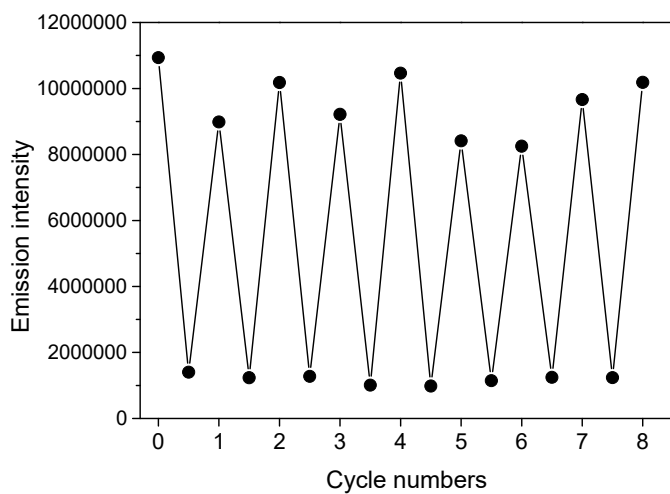


Fig. S13 The emission intensity of the thin films of **1** ($1M_s$) at 631 nm upon fuming and removal of ammonia vapor over 8 cycles.

8. References

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