

Supporting Information for:

**A twisted-intramolecular-charge-transfer (TICT)
based ratiometric fluorescent thermometer with a
mega-Stokes shift and a positive temperature
coefficient**

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Materials and Instruments: Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker 400 spectrometer, using TMS as an internal standard. Chemical shifts were given in ppm and coupling constants (J) in Hz. Mass spectrometry data were obtained with a HP1100LC/MSD mass spectrometer and a LC/Q-TOF MS spectrometer. UV—vis absorption spectra were collected on an Agilent Cary 60 UV-Vis Spectrophotometer. Fluorescence measurements were performed on a VAEIAN CARY Eclipse fluorescence spectrophotometer equipped with a Single Cell Peltier temperature controller. For temperature dependence studies, the cuvettes were tightly sealed with a cap to prevent solvent evaporation; the temperature was held for 20—30 min to ensure that the solution in the cuvettes reached thermal equilibrium before data collection.

Fluorescent quantum yields were determined using quinine sulfate (in 0.05 M H_2SO_4) as a reference.¹ The quantum yield was calculated according to Equation 1:

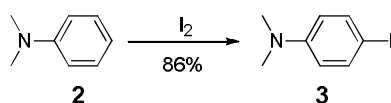
$$\Phi_{F(x)} = \frac{A_s \int emission_x \left(\frac{n_x}{n_s}\right)^2}{A_x \int emission_s} \Phi_{F(s)} \quad (\text{Equation 1})$$

where Φ_F represents the fluorescence quantum efficiency, A the absorbance at the excitation wavelength, $\int emission$ the area under the fluorescence spectrum, and n the refractive index of the solvent in use. Subscripts s and x indicate the reference standard and the unknown, respectively.¹

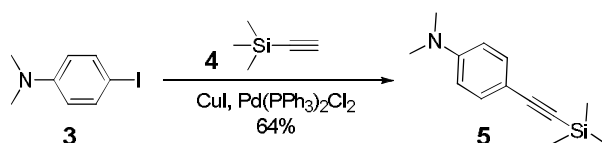
Computational Details: Quantum-chemical calculations were performed on **1** using Gaussian 09.² Becke's three-parameter and Lee-Yang-Parr hybrid functional (B3LYP)³⁻⁵ and a 6-31+G(d,p) basis set⁶ were used.

The geometry of **1** was optimized in DMSO using the polarizable continuum model (PCM) to act as an implicit solvent incorporation.^{7, 8} Following this, TD-DFT calculations were carried out on the optimized molecular structure in order to determine the photoexcitation mechanism of **1**.

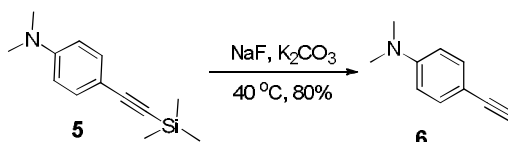
Synthesis:



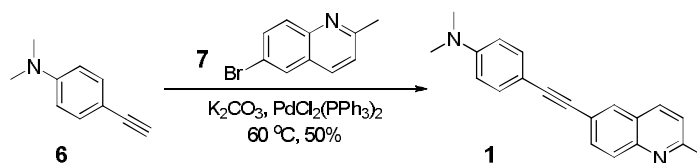
Resublimed iodine (4.28 g, 16.8 mmol) was added in small portions over 45 min to a mixture of *N,N*-dimethylaniline (2.37 mL, 18.7 mmol) and NaHCO₃ (2.35 g, 27.9 mmol) in 16 mL water between 12 and 15 °C. The mixture was warmed up to room temperature (RT) and kept for 10 min. This mixture was then diluted with 500 mL ether, and the organic liquid was extracted consecutively with 50 mL water, 100 mL sodium thiosulfate, and another 100 mL water. The organic layer was dried with Na₂SO₄, concentrated, and evaporated to give product **3**.⁹ Yield: 3.98 g (86%). Mp: 63.5-66.1 °C.



Compound **3** (2.47 g, 10 mmol), Pd(PPh₃)₂Cl₂ (0.035 g, 0.05 mmol), CuI (0.1 g), triethylamine (50 mL), PPh₃ (0.052 g, 0.2 mmol) and ethynyltrimethylsilane (1.6 ml, 11.3 mmol) were added to a round-bottomed flask (100 mL). The resulted mixture was stirred at RT for 5 h, and then filtered to remove salts, before the addition of 100 ml CH₂Cl₂. The extracted organic layer was dried over Na₂SO₄ to yield **5**.⁹ Yield: 1.4 g (64%).



Following a general deprotection procedure, the mixture of **5** (4.35 g, 20 mmol) with sodium fluoride (2.09 g, 5 mmol) and K₂CO₃ (6.9 g, 5 mmol) in MeOH/THF (60 mL, 1:1, v/v) was heated at 40 °C for 4 h. After cooling to room temperature, the mixture was filtered to remove salts and evaporated to yield **6** as an orange solid.¹⁰ Yield: 2.32 g (80%).



A mixture of **6** (2.17 g, 15 mmol), 6-bromo-2-methylquinoline (**7**) (2.2 g, 10 mmol), Pd(PPh₃)₂Cl₂ (0.04 g, 0.056 mmol) and Et₃N (3 ml, 20 ml) in dimethylformamide (20

ml) was heated at 60 °C for 24 h. After cooling to RT, the mixture was filtered to remove salts, followed by the addition of 100 ml H₂O. The resulting mixture was extracted with ethyl acetate (EA; 50 ml × 3). The organic solution was combined and dried with Na₂SO₄ to yield a crude product. This product was recrystallised in EA/petroleum ether to give **1**. Yield: 1.43 g (50%).

¹H-NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.94 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.90 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.75 (dd, *J* = 8.8, 1.6 Hz, 1H, Ar-H), 7.44 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.28 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.67 (d, *J* = 8.8 Hz, 2H, Ar-H), 2.99 (s, 6H, CH₃), 2.73 (s, 3H, CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ 159.24, 150.26, 147.03, 135.71, 132.82, 132.27, 130.04, 128.60, 126.35, 122.50, 121.63, 111.87, 109.82, 91.67, 87.23, 77.34, 77.02, 76.70, 40.18, 25.37. HRMS(ESI) calcd for C₂₀H₁₉N₂ [MH⁺] 287.1548, found 287.1542.

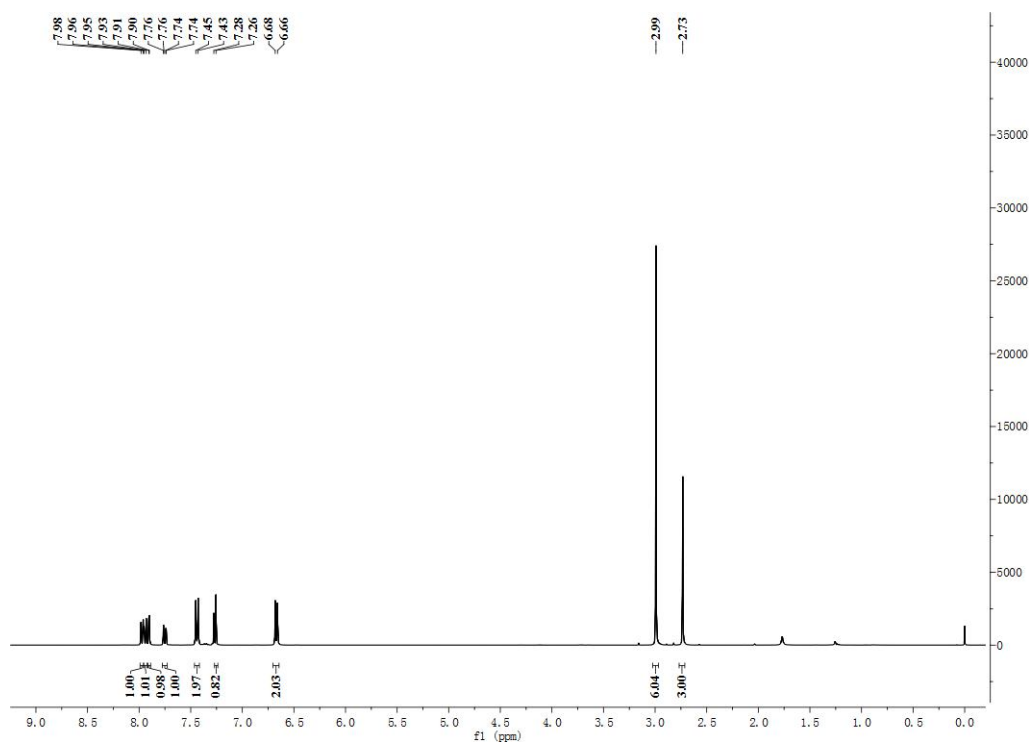


Fig. S1. ¹H-NMR spectra of **1** in CDCl₃.

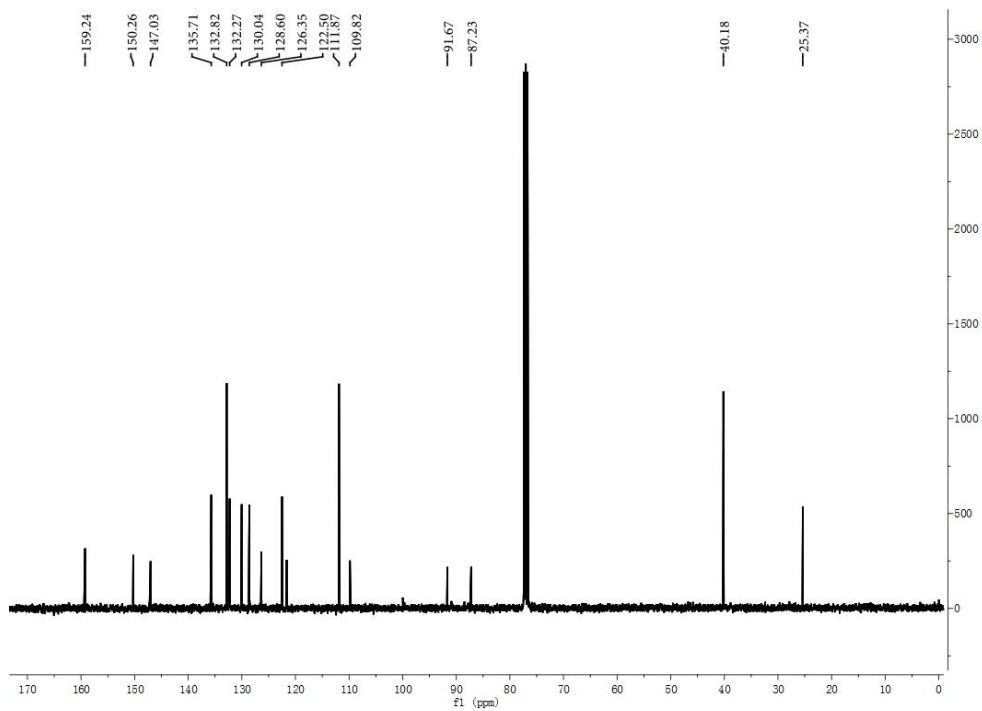


Fig. S2. ^{13}C -NMR spectra of **1** in CDCl_3 .

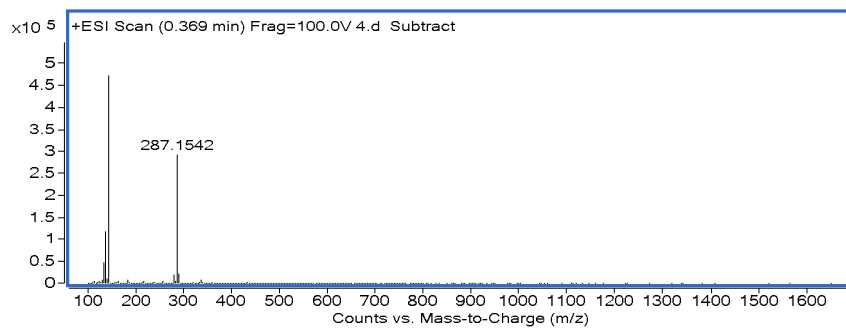


Fig. S3. MS spectrum of **1**.

Table S1. Spectral intensity maxima of UV-vis absorption and fluorescence [λ (nm) and ν (cm^{-1})], molar extinction coefficients [ϵ ($\times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$)], at the peak UV—vis absorption wavelengths] and emission quantum yields (ϕ) of **1** at 25 °C in various solvents, and the associated relative dielectric constants (ϵ_r), refractive indices (n), and orientation polarisability (Δf and $\Delta f'$) of those solvents.^a

S/N	solvent	absorption		emission		ϵ	ϕ	ϵ_r	n	Δf	$\Delta f'$
		λ_{abs}	ν_{abs}	λ_{em}	ν_{em}						
1	acetone	334	29940	515	19417	2.75	0.119	21.36	1.359	0.285	0.762
2	acetonitrile	332	30120	540	18519	2.91	0.143	35.94	1.344	0.305	0.815
3	<i>n</i> -Butanol	335	29851	474	21097	2.27	0.021	17.51	1.397	0.264	0.726
4	chloroform	335	29851	461	21692	2.70	0.529	4.89	1.446	0.150	0.431
5	dichloromethane	335	29851	481	20790	2.74	0.456	9.02	1.424	0.218	0.600
6	DMF	335	29851	536	18657	2.36	0.220	37.06	1.430	0.275	0.794
7	DMSO	338	29586	546	18315	2.50	0.189	46.71	1.479	0.263	0.797
8	1,4-dioxane	334	29940	439	22779	2.86	0.737	2.27	1.422	0.027	0.170
9	ethanol	334	29940	493	20284	2.55	0.009	24.55	1.359	0.290	0.777
10	ethyl acetate	332	30120	466	21459	2.97	0.552	6.03	1.372	0.200	0.513
11	<i>n</i> -Hexane	332	30120	380	26316	2.66	0.617	1.886	1.375	-0.001	0.114
12	methanol	334	29940	496	20161	2.54	0.006	32.66	1.327	0.309	0.812
13	tetrahydrofuran	334	29940	472	21186	2.77	0.471	7.47	1.406	0.209	0.560
14	toluene	334	29940	420	23810	2.77	0.654	2.43	1.497	0.018	0.176

^a The relative dielectric constants (ϵ_r) and refractive indices (n) of various solvents are imported from ref. 11 for non-alcoholic solvents, and ref. 12 for alcoholic solvents.

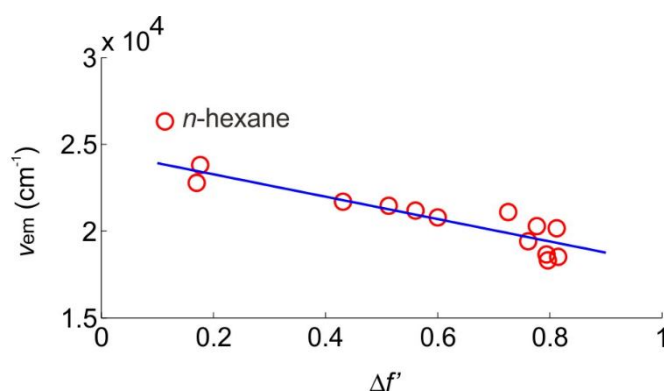


Fig. S4. The Lippert-Mataga plot for the fluorescence transition energies of **1**, against $\Delta f'$.

Table S2. Fluorescence quantum yields of **1** in DMSO and ethyl acetate at different temperatures.

Temp. Sol.	25 °C	35 °C	45 °C	55 °C	65 °C
DMSO	0.189	0.193	0.205	0.210	0.223
Ethyl Acetate	0.552	0.543	0.528	0.494	0.489

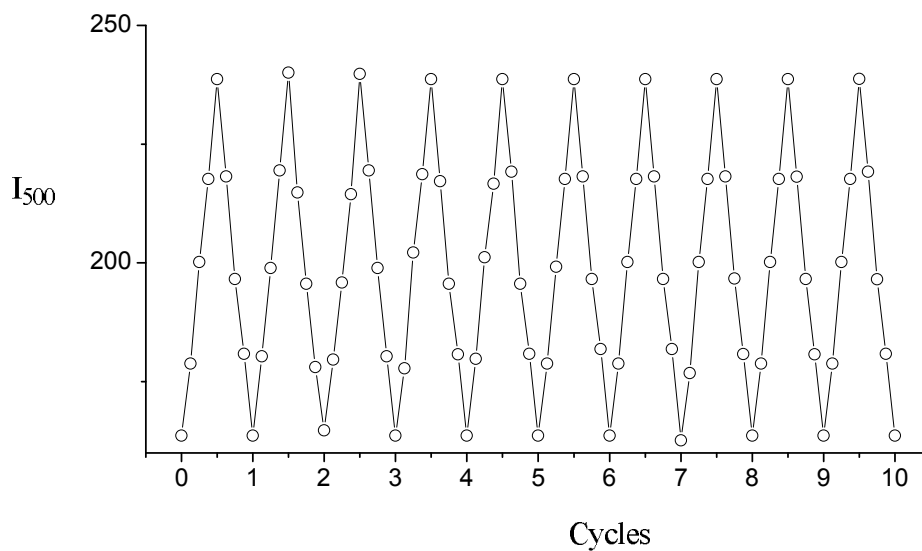


Fig. S5. A reversibility study of the fluorescence intensities of **1** during 10 heating/cooling cycles in DMSO. Fluorescence intensities were monitored at 500 nm.

Reference:

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