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Electronic Supplementary Information for

Selective and visual Ca^{2+} ion recognition in solution and in a self-assembly organogel of terpyridine-based derivative

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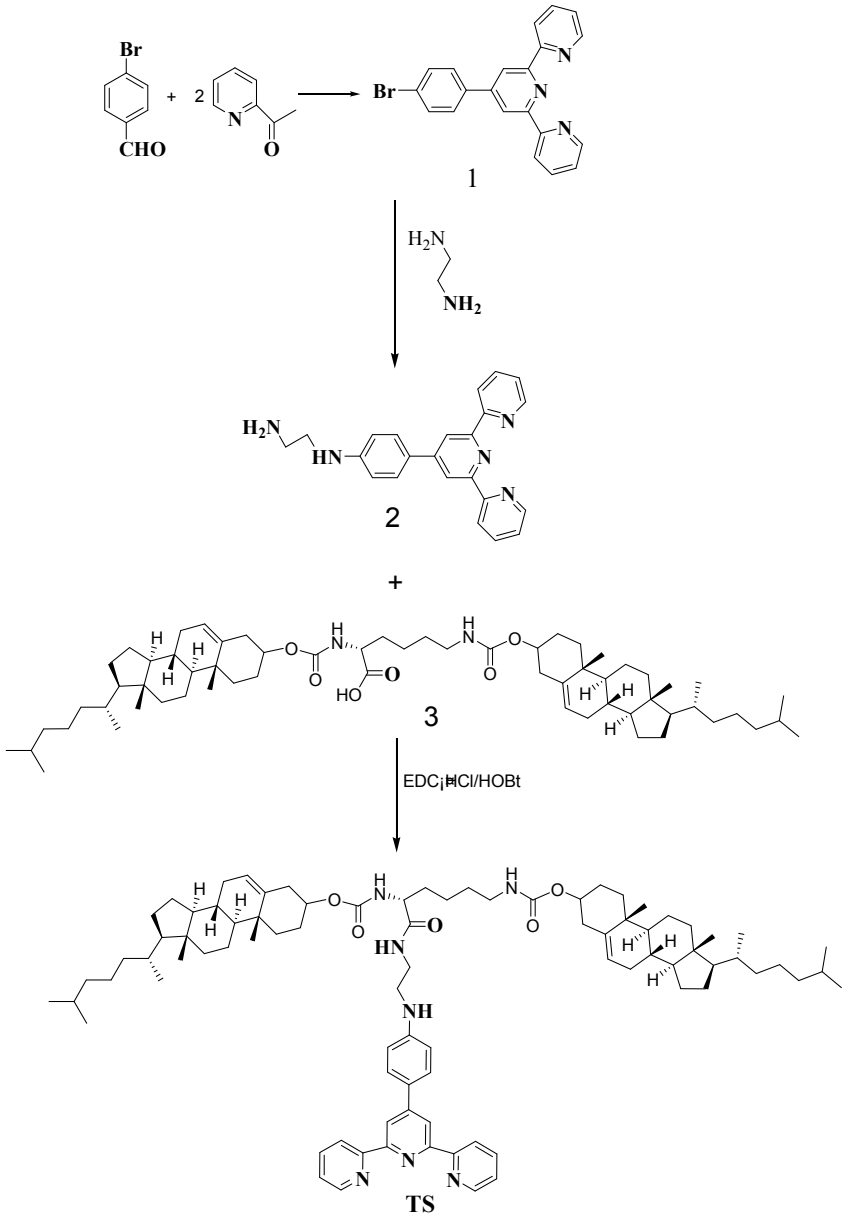
1. Synthesis of TS



Scheme S1. The synthesis of **1** and **3** could be seen in literature 1 and 2 respectively.

Synthesis of **2**

4'-(p-Bromophenyl)-2,2':6',2''-terpyridine (1 g, 2.6 mmol) and ethanediamine (7.2 g, 13 mmol) were added into ethanol (70 mL) and refluxed for16 h. The solution was evaporated and purified by chromatography using CH_2Cl_2 and MeOH (10:1) as eluent, resulting in white crystal (0.76g, 80%). M.p. > 300 °C. ^{1}HNMR: 3.0(t, 2H, J=5 Hz), 3.25-3.26 (t, 2H, J=5 Hz), 6.73-6.75 (d, 2H, J=8 Hz), 7.32-7.34 (t, 2H, J=5.5 Hz), 7.81-7.82 (d, 2H, J=8 Hz), 7.85-7.88 (t, 2H, J=7 Hz), 8.65-8.73 (m, 6H). HRMS

calc. for $[C_{23}H_{21}N_5+Na]^+$: 390.1695; Found: 390.1665.

Synthesis of **TS**

To a mixture of compound **2** (2mmol, 0.73 g) , compound **3** (1.94 g, 2mmol) , EDC•HCl（1.15g, 6mmol）, HOBt（0.81g, 6mmol）and triethylamine (6.0 mL) in $CHCl_3$ (20mL) was stirred at room temperature for 24 hrs. After evaporated solvent and washed with water, the separated solid was filtered . The crude product was subjected to column chromatography using dichloromethane: methanol (20:1) as eluent to afford the pure pink powder. M.p. 98-100 °C. ^{1}HNMR (500 M, DMSO-d_6, δ): 0.50 (s, 3H, CH_3), 0.64 (s, 3H, CH_3), 0.81-2.29 (m, 91H), 3.10-3.13 (t, 2H), 3.30-3.35 (t, 2H), 3.50-3.64 (t, 2H), 4.77 (t, 1H), 5.64-5.65 (m, 1H), 6.72-6.73 (d, 2H, J=8 Hz), 7.32-7.34 (d, 2H, J=6 Hz), 7.80-7.82 (d, 2H, J=8 Hz), 7.84-7.87 (t, 2H, J=7.5 Hz), 8.66-8.68 (d, 2H, J=8 Hz), 8.70 (s, 2H), 8.72-8.73 (d, 2H, J=4Hz). ^{13}CNMR (125 M, $CDCl_3$, δ): 173.05, 156.92, 156.48, 155.56, 149.94, 149.23, 149.05, 139.69, 136.81, 128.26, 126.61, 123.66, 122.71, 122.58, 121.36, 117.43, 112.94, 74.99, 74.53, 56.70, 56.43, 56.27, 56.02, 55.234, 49.88, 49.79, 43.59, 42.29, 42.19, 39.76, 39.53, 38.82, 38.57, 36.96, 36.79, 36.47, 36.20, 35.84, 35.77, 31.86, 31.77, 30.32, 29.69, 29.36, 29.23, 28.23, 28.17, 28,12, 28.03, 27.96, 24.23, 23.96, 23.88, 22.84, 22.57, 22.16, 21.02, 20.89, 19.31, 18.67, 14.12, 11.82, 11.78. HRMS calc. for $[C_{85}H_{121}N_7O_5]^+$: 1320.9507; Found: 1320.9511.

2. Other experiment data

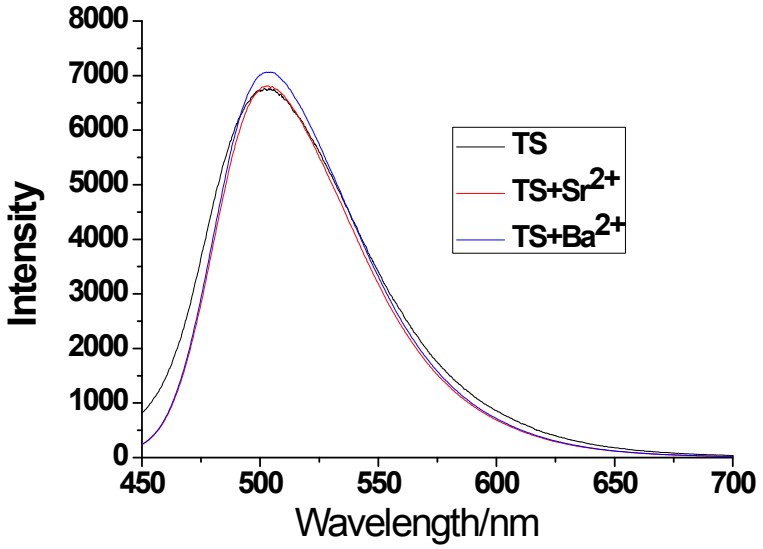


Fig. S1 Fluorescence emission spectrum changes of TS (10^{-5} M) upon the addition of Sr^{2+} and Ba^{2+} (50 eq.).

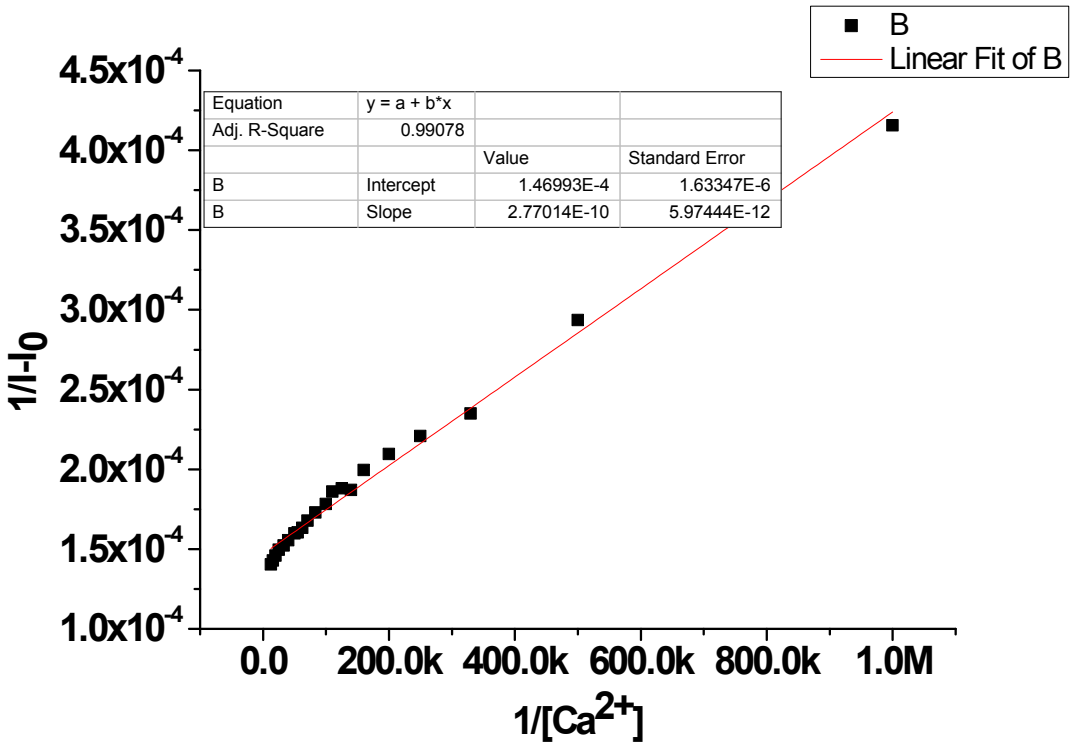


Fig. S2 The linear fitting curve of fluorescence change of **TS** (10^{-5}M) with the addition of $[Ca^{2+}]$.

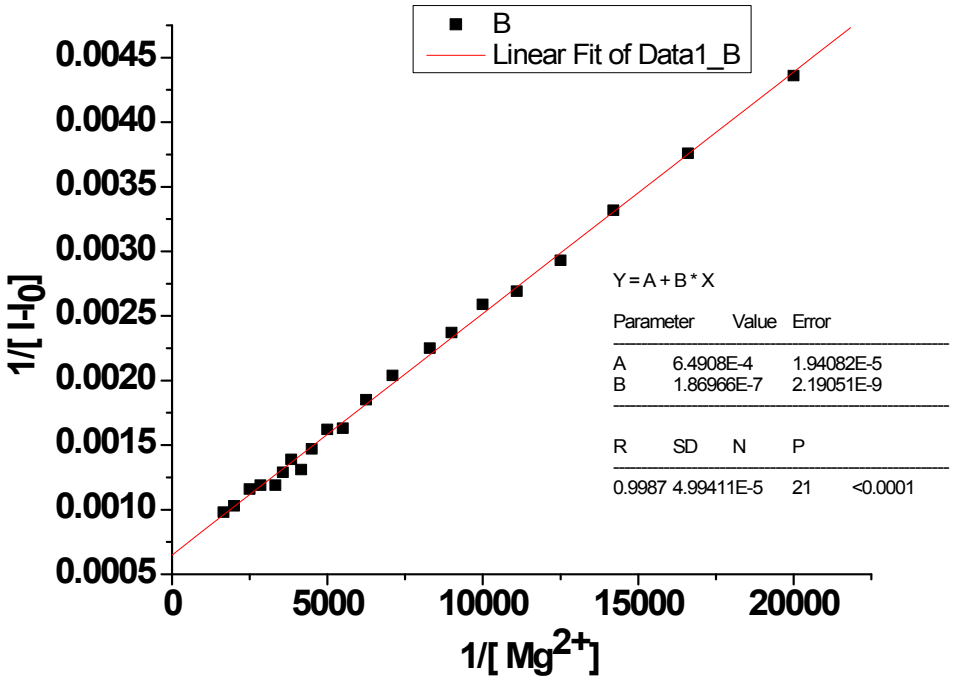


Fig. S3 The linear fitting curve of fluorescence change of **TS** (10^{-5} M) with the addition of [Mg^{2+}].

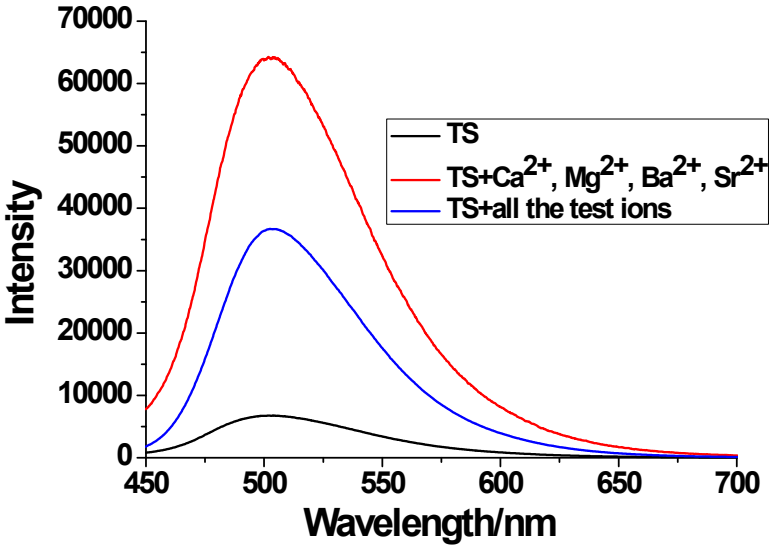


Fig. S4 the fluorescent changes of **TS** upon the addition of mixed ions (50 eq.).

Detection limit of **TS** toward Ca^{2+} and Mg^{2+} by fluorescence intensity changes at 502nm

n	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Intensity (X_n)	134.2	141.3	141.7	142.1	141.4	140.5	142.1	141.7	142.3	141.7	142.4)	139.6	142.6	142.5	142.4
n	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Intensity (X_n)	142	142.4	143	143	142.8	142.6	139.4	143	143.1	143.4	144.2	139.7	140	140	140.8

$X_{average} = 141.5$ $\sigma_{wb} = sqrt(\Sigma(x_n - x_{average})^2/n) = 1.814$

$n > 20$, $L = 4.6\sigma_{wb} = 4.6\times1.814 = 8.344$

$K_{ca} = 5.3\times10^5$ $\boldsymbol{\varepsilon} = 1/L_0A = 4.33\times10^8$ M R = 0.9907

The detection limit: $[Ca^{2+}] = L/\varepsilon = 8.344/4.33\times10^8 = 1.93\times10^{-8}$ M

$K_{ca} = 3.44\times10^3$ $\boldsymbol{\varepsilon} = 1/L_0A = 6.4\times10^5$ M R = 0.9987

The detection limit: $[Mg^{2+}] = L/\varepsilon = 1.30\times10^{-5}$ M

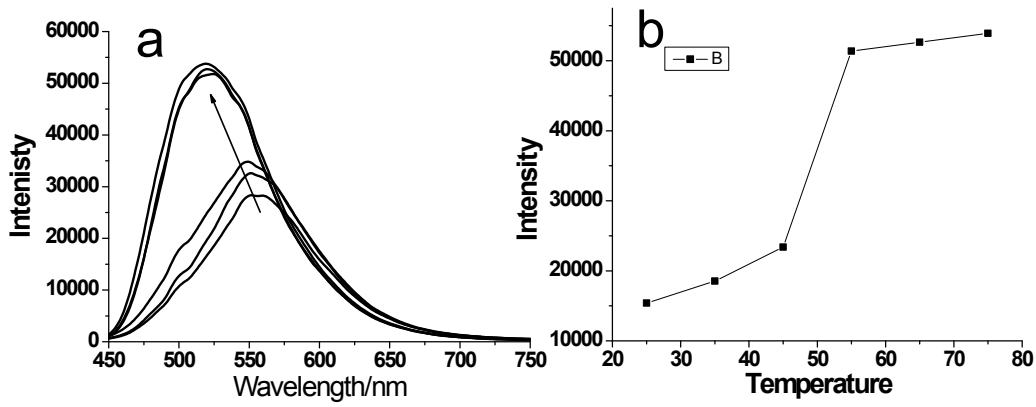


Fig. S5 Temperature dependent fluorescence changes of **TS** gel (25 mg/mL) and Ca^{2+} (10 eq.) with gel-to-suspension transformation; b) b) the temperature dependent changes of fluorescent peaks at 516 nm, Unit: °C.

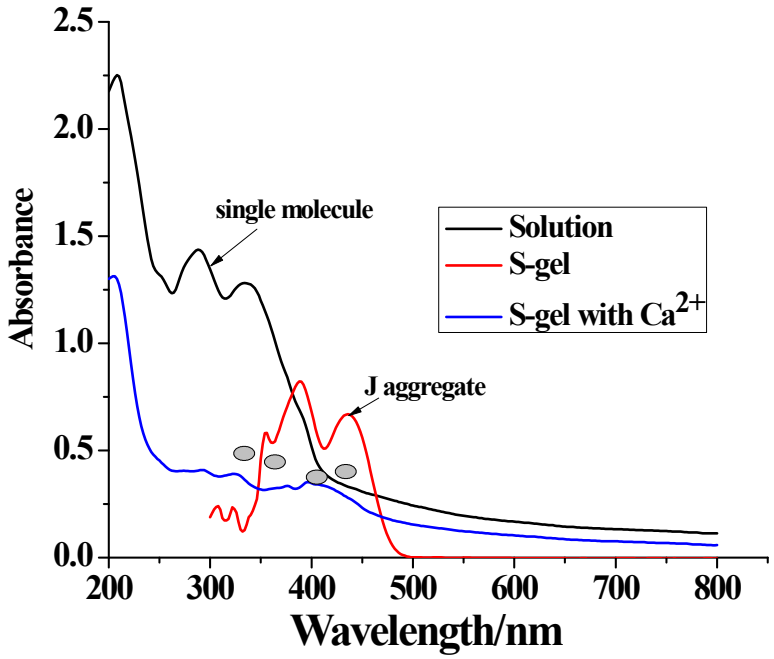


Fig. S6 The UV-vis spectra of solution, S-gel and S-gel with Ca^{2+} of **TS**.

References

1. X. Piao, Y. Zou, J. C. Wu and Tao Yi, *Org. Lett.,* 2009, **11**, 3818-3821.
2. X. D. Yu, X. H. Cao, L. M. Chen, H. C. Lan, B. Liu and T. Yi, *Soft Matter,* 2012, **8**, 3329-3334.