A 5.3 nm giant Metal-organic cage and its Supramolecular Gel for the Formation of Dye Molecular Ionic Pairs

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1. General procedures

NMR spectra were recorded on a Bruker ADVANCE 400 or 500 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard.

Mass spectra of complexes and ligands were determined on Waters Synapt G2 Mass Spectrometer with traveling wave ion mobility (TWIM) under the following conditions: ESI capillary voltage, 3.5 kV; cone voltage, 35 V; desolvation gas flow, 800 L/h. TWIM-MS was measured with IM traveling wave height, 25 V; and IM traveling wave velocity, 1000 m/s.

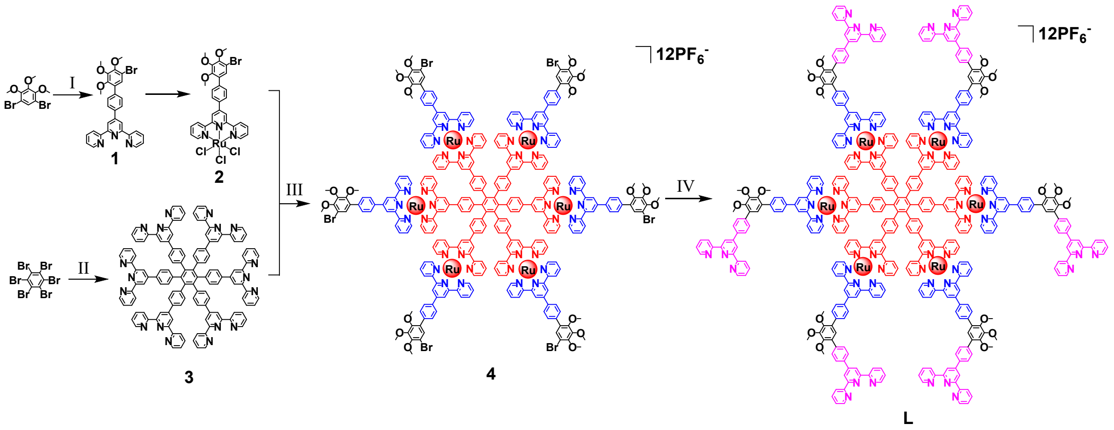
Atomic force microscopy (AFM) was conducted on a Bruker Dimension Icon AFM system with ScanAsyst and the data were processed by NanoScope Analysis version 1.5 (Bruker Software, Inc.). AFM samples were prepared by casting a sample solution (1×10^{-7} M) on a freshly cleaved mica surface.

The transmission electron microscope (TEM) images were recorded on a JEM 2100 transmission electron microscope operated at an accelerating voltage of 200 KV. TEM samples were prepared by drop-casting a sample solution (1×10^{-7} M) onto a carbon-coated copper grid and dried in vacuo for 24 h.

Absorption spectra were measured with Hitachi (model U-3010) UV–vis spectrophotometer in a 1-cm quartz cell. Emission spectra were measured with Hitachi (F-7000) fluorescence spectrophotometer in a 1-cm quartz cell.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. The 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine [1] were synthesized according to the literature procedures.

2. Synthesis and characterization.



Scheme S1 Synthesis of ligands **L**. Reagents and conditions: (I) 4'-(4-boronatophenyl)[2,2':6',2'']terpyridine, $Pd(PPh_3)_4$, K_2CO_3, THF, N_2, reflux; (II) 4'-(4boronatophenyl)[2,2':6',2'']terpyridine, $Pd(PPh_3)_4$, Na_2CO_3, N_2, PhMe/H2O/t-BuOH (3:3:1, v/v/v), reflux; (III) $CHCl_3/CH_3OH$(1:1, v/v), N-ethyl morpholine, reflux; (IV) 4'-(4-boronatophenyl)[2,2':6',2'']terpyridine, $Pd(PPh_3)_4$, K_2CO_3, CH_3CN/CH_3OH(2:1, v/v), N_2 , reflux;.

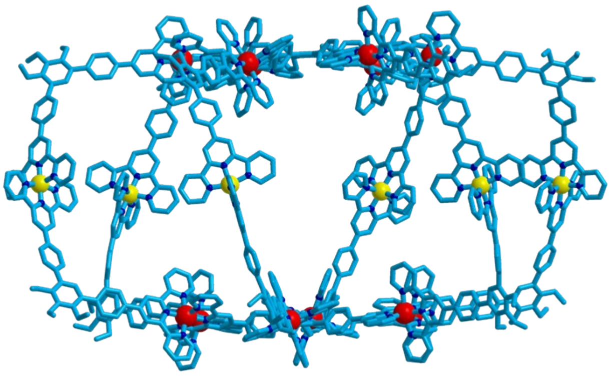
Compound 1 [2]: To a mixture of 1,5-dibromo-2,3,4-trimethoxybenzene (3.00g, 8.77mmol) and 4'-(4-boronatophenyl)[2,2':6',2'']terpyridine (3.10g, 8.77mmol) in THF (100 mL) , K_2CO_3 (3.03g, 21.93mmol) was added. The system was pumped and backfilled with nitrogen; then $Pd(PPh_3)_4$ (600 mg) was added. After refluxing for 24 h under nitrogen, the mixture was cooled to 25 °C and evaporated under reduced pressure, then the residue was purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/PE (1:1, v/v) to give a white solid 2.90g (60%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$, ppm) δ 8.81 (s, 2H), 8.77-8.76 (d, 2H), 8.72-8.71 (d, 2H), 8.00-7.98 (d, 2H), 7.94-7.90 (d, 2H), 7.67-7.65 (d, 2H), 7.41-7.38 (m, 3H), 4.02 (s, 3H), 3.99 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 156.22, 155.98, 151.13, 150.75, 149.85, 149.17, 147.95, 137.58, 137.51, 136.95, 132.07, 129.61, 128.02, 127.28, 123.91, 121.41, 118.82, 111.85, 61.37, 61.18, 61.11.

Compound 2: Compound **1** (1.00g, 1.82 mmol) and $RuCl_3·3H_2O$ (565.9 mg, 2.16 mmol) was suspended in $CHCl_3$/MeOH(1:1, v/v) (80 mL); After stirred for 8 h at room temperature, The mixture were heated up to 75°C and stirred for 1 d, then cooled to 25 °C and filtered to obtain a brown powder. The solid was washed with MeOH repeatedly until the filtrate get clean and colorless, the solid was collected and dried in vacuum for 12 h to get the desired compound, it was used directly for the next step without further purification: 1.26 g, 91 %.

Compound 3 [3]: To a flask containing perbromobenzene (500 mg, 0.91 mmol), 4'-(4-boronatophenyl)[2,2':6',2'']terpyridine (2.31 g, 6.53 mmol) and Na_2CO_3 (1.16 g, 10.88 mmol), a mixed solvent (84 mL) of PhMe/H_2O/t-BuOH (3:3:1, v/v/v) was added. After $Pd(PPh_3)_4$ (387 mg, 327 μmol) was added, the system was pumped and backfilled with nitrogen. Then the mixture was refluxed for six days under N_2. After cooled to 25 °C, the mixture was extracted with $CHCl_3$ and the combined organic extract was evaporated to dryness in vacuo to give a reside that was washed with MeOH, then subjected to column chromatography (Al_2O_3, CH_2Cl_2/MeOH = 100:1) and then recrystallized from a mixture of $CHCl_3$/MeOH to give compound **3**, as a white solid: 1.10g (63%); ^{1}H NMR (500 MHz, 298 K, $CDCl_3$, ppm) δ 8.59-8.57 (m, 24H), 8.53-8.51 (d, 12H), 7.78-7.74 (d, 12H), 7.60-7.58 (d, 12H), 7.25-7.21 (d, 12H), 7.17-7.15 (d, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.36, 155.59, 149.62, 148.95, 141.27, 140.28, 136.56, 135.26, 131.89, 126.03, 123.47, 121.18, 118.75.

Complex 4: The compound **3** (25mg, 0.013mmol) and compound **2** (80mg, 0.11mmol) was added to a 100 mL flask, then 60 ml $CHCl_3$/CH_3OH(1:1, v/v) was added as solvent. After adding 4 drops N-ethyl morpholine, the suspension was stirred at 80 °C for six days. After cooled to ambient temperature. The solution was evaporated under reduced pressure, then the residue was purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/CH_3OH to give a red solid, which was dissolved in CH_3OH and precipitated with NH_4PF_6 to afford complex **4**, as a dark red solid (78mg, 80 %);^{1}H NMR (500 MHz, 298 K, CD_3CN, ppm) δ= 9.03 (s, 12H), 8.98 (s, 12H), 8.67-8.65 (d, 12H), 8.62-8.60 (d, 12H), 8.26-8.24(d, 12H), 8.12-8.10 (d, 12H), 7.87-7.71 (m, 36H), 7.68 (t, 12H), 7.49(s, 6H), 7.38-7.36 (d, 12H), 7.34 (d, 12H), 7.06 (t, 12H), 6.90 (t, 12H), 3.99 (s, 18H), 3.95 (s, 18H), 3.76(s,18H); ESI/MS (*m/z*): 2386.63 [**M**-3PF_6^-]$^{3+}$ (calcd. *m/z* = 2386.81), 1753.98 [**M**-4PF_6^-]$^{4+}$ (calcd. *m/z* = 1753.87), 1374.21 [**M**-5PF_6^-]$^{5+}$ (calcd. *m/z* = 1374.10), 1120.89 [**M**-6PF_6^-]$^{6+}$ (calcd. *m/z* = 1120.92), 940.06 [**M**-7PF_6^-]$^{7+}$ (calcd. *m/z* = 940.08), 804.43 [**M**-8PF_6^-]$^{8+}$ (calcd. *m/z* = 804.45) , 698.93 [**M**-9PF_6^-]$^{9+}$ (calcd. *m/z* = 698.96). Elemental Analysis (**4**+nNH_4PF_6, contains a small amount of NH_4PF_6 salt): Calcd. **4**+2NH_4PF_6 ($C_{312}H_{236}Br_6F_{84}N_{38}O_{18}P_{14}Ru_6$): C, 48.51%; H, 3.08%; N, 6.89%. Found: C, 48.81%; H, 3.45%; N, 6.41%.

L: To a mixture of complex **4** (42mg, 0.0055mmol) and 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine (14mg, 0.040mmol) in 60ml CH_3CN/CH_3OH(2:1, v/v), K_2CO_3 (13.8mg, 0.10mmol) was added. The system was pumped and backfilled with nitrogen; then $Pd(PPh_3)_4$ (10 mg) was added. After refluxing for six days under nitrogen, the mixture was cooled to 25 °C and evaporated under reduced pressure. The solid was washed with CH_3OH, then excess NH_4PF_6 was added to afford an red precipitate, which was thoroughly washed by CH_3OH and water to give the desired **L** as a red solid (22 mg, 45%).^{1}H NMR (500 MHz, 298 K, CD_3CN, ppm) δ= 9.07 (s, 12H), 8.97 (s, 12H), 8.84 (s, 12H), 8.72 (m, 24H), 8.65-8.63 (m, 24H), 8.29 (d, 12H), 8.11 (d, 12H), 8.01 (m, 36H), 7.85 (m, 36H), 7.68 (t, 12H), 7.48(t, 12H), 7.37 (m, 30H), 7.08 (t, 12H), 6.91 (t, 12H), 4.07 (s, 18H), 3.87 (s, 18H), 3.84(s,18H); ESI/MS (*m/z*): 2096.49 [**M**-4PF_6^-]$^{4+}$ (calcd. *m/z* = 2096.42), 1648.41 [**M**-5PF_6^-]$^{5+}$ (calcd. *m/z* = 1648.14), 1349.37 [**M**-6PF_6^-]$^{6+}$ (calcd. *m/z* = 1349.29), 1135.92 [**M**-7PF_6^-]$^{7+}$ (calcd. *m/z* = 1135.83), 975.83 [**M**-8PF_6^-]$^{8+}$ (calcd. *m/z* = 975.73) , 851.18 [**M**-9PF_6^-]$^{9+}$ (calcd. *m/z* = 851.21). Elemental Analysis (**L**+nNH_4PF_6, contains a small amount of NH_4PF_6 salt): Calcd. **L**+NH_4PF_6 ($C_{438}H_{316}F_{78}N_{55}O_{18}P_{13}Ru_6$): C, 57.63%; H, 3.49%; N, 8.44%. Found: C, 57.68%; H, 3.71%; N, 7.91%.



S

Scheme S2 Representative energy-minimized structures from molecular modeling of metallo-supramolecular **S** (The molecular structure simulation of **S** was completed in Material Studio-Calculation-Geometry Optimization).

Table S1. The parameters of **S** structure optimization and the results of energy optimization.

Geometry optimization parameters	Energy parameters	Final structure
Algorithm: Smart Convergence tolerance: Energy: 0.001 kcal/mol Force: 0.5 kcal/mol/A Maximum number of iterations: 5000 Motion groups rigid: NO	Forcefield: Universal Charges: Use current Electrostatic terms: Summation method: Atom based Truncation method: Cubic spline Cutoff distance: 12.5 A Spline width: 1 A Buffer width: 0.5 A van der Waals terms: Summation method: Atom based Truncation method: Cubic spline Cutoff distance: 12.5 A Spline width: 1 A Buffer width: 0.5 A	Total energy: 5333.429007 kcal/mol Contributions to total energy (kcal/mol): Valence energy (diag. terms): 3856.398 Bond: 424.563 Angle: 2949.182 Torsion: 480.528 Inversion: 2.125 Non-bond energy: 1477.031 Van der Waals: 1477.031 Electrostatic: 0.000 rms force: 3.115E-002 kcal/mol/A max force: 2.644E-001 kcal/mol/A

S: L (20mg, 0.00223mmol) with $Zn(NO_3)_2{\cdot}4H_2O$ (2mg, 0.00669mmol) in a precise 1:3 molar ratio in CH_3CN/CH_3OH(2:1, v/v) (21mL) and stirring at 75 °C for 12 h. Followed by cooling to 25 °C, the water (20mL) and the excess NH_4PF_6. There will be red suspended solids in the solvent, then, after suction filtration, clean the excess NH_4PF_6 with water and methanol to obtain red solid **S**. ^{1}H

NMR (500 MHz, 298 K, CD_3CN, ppm) δ= 9.10 – 8.98 (m, 72H), 8.75 (d, 24H), 8.65 (d, 48H), 8.31 (s, 48H), 8.18 (s, 72H), 8.00 (d, 48H), 7.80 (d, 96H), 7.37 (dd, 84H), 7.10 (s, 24H), 6.87 (s, 24H), 4.10 (s, 36H), 3.92 (d , 72H). ESI-MS (*m/z*): 1679.164 [**M**-11PF_6^-]$^{11+}$ (calcd. *m/z* = 1678.920), 1526.991 [**M**-12 PF_6^-]$^{12+}$ (calcd. *m/z* = 1526.930), 1398.223 [**M**-13PF_6^-]$^{13+}$ (calcd. *m/z* = 1398.320), 1288.357 [**M**-14PF_6^-]$^{14+}$ (calcd. *m/z* = 1288.080), 1192.664 [**M**-15PF_6^-]$^{15+}$ (calcd. *m/z* = 1192.540), 1109.197 [**M**-16PF_6^-]$^{16+}$ (calcd. *m/z* = 1108.950), 1035.306 [M-17PF_6^-]$^{17+}$ (calcd. *m/z* = 1035.180), 969.728 [**M**-18PF_6^-]$^{18+}$ (calcd. *m/z* = 969.619), 911.160 [**M**-19PF_6^-]$^{19+}$ (calcd. *m/z* = 910.955), 858.266 [**M**-20PF_6^-]$^{20+}$ (calcd. *m/z* = 858.158), 810.542 [**M**-21PF_6^-]$^{21+}$(calcd. *m/z* = 810.388).

3. ^{1}H NMR, ^{13}C NMR, 2D COSY NMR, 2D NOESY NMR.

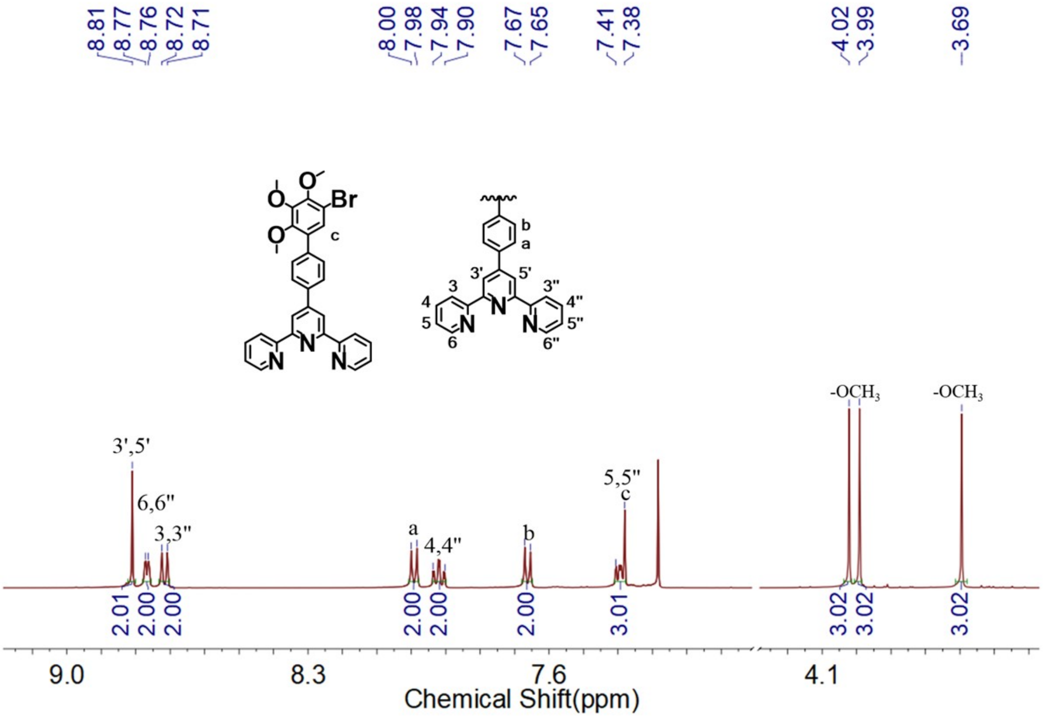


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

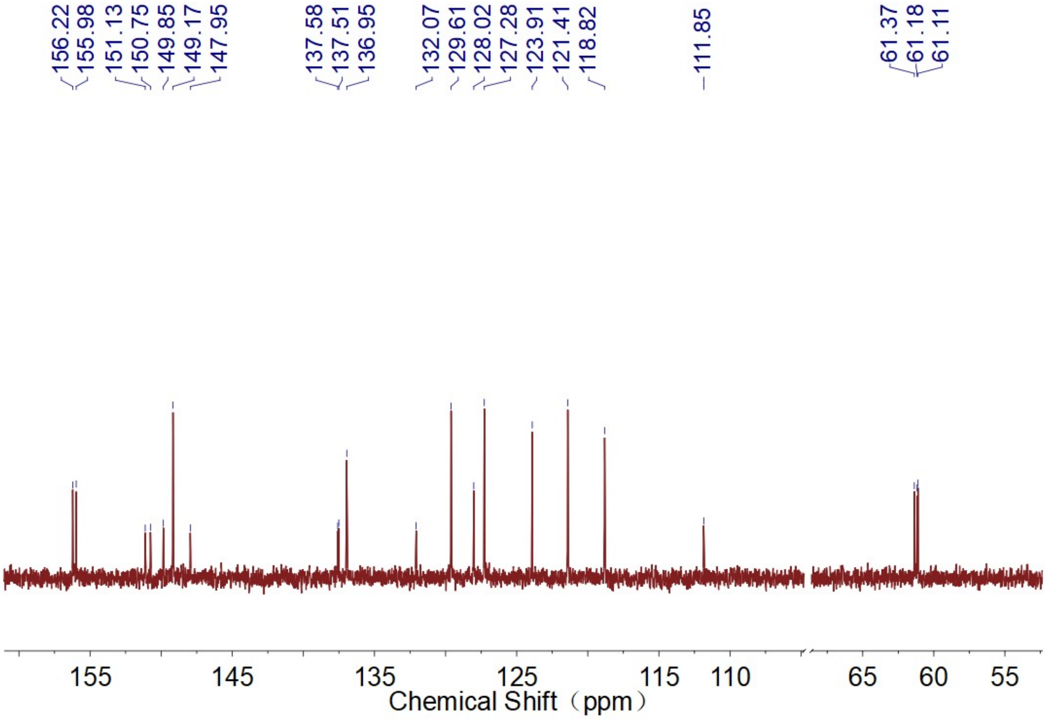


Figure S2. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

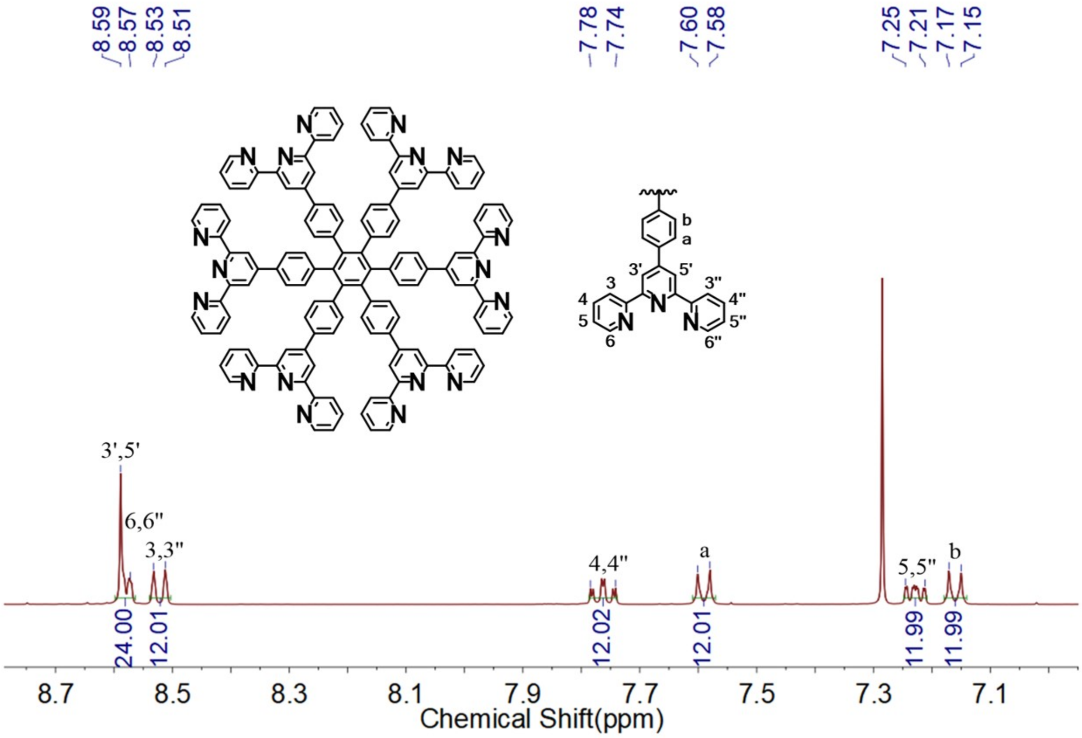


Figure S3. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

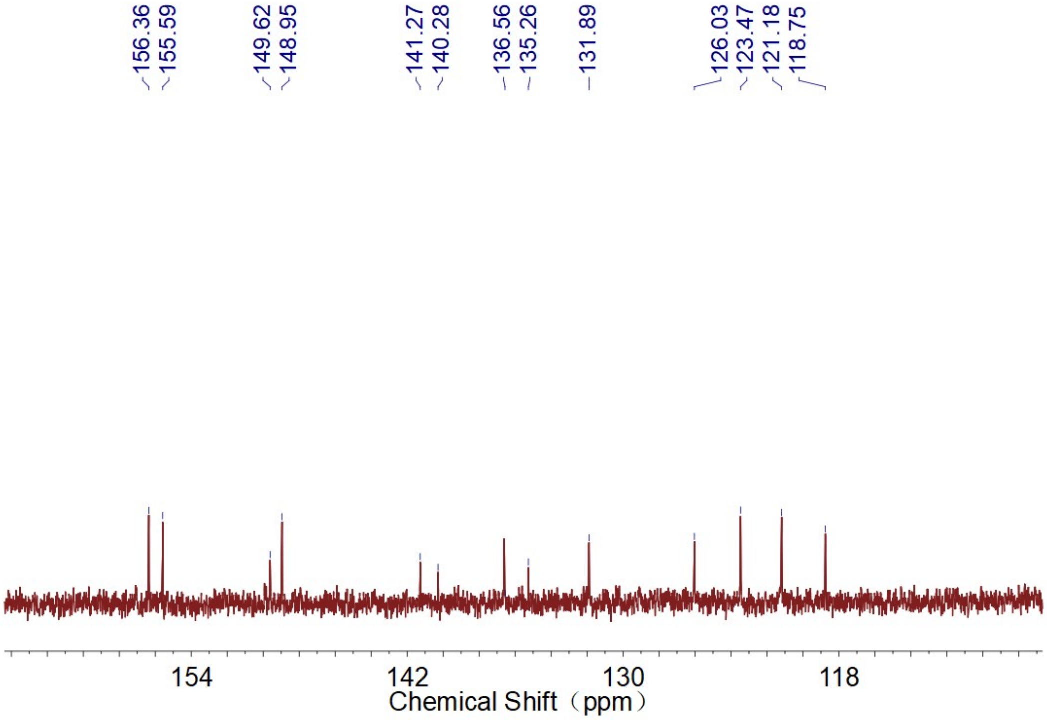


Figure S4. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

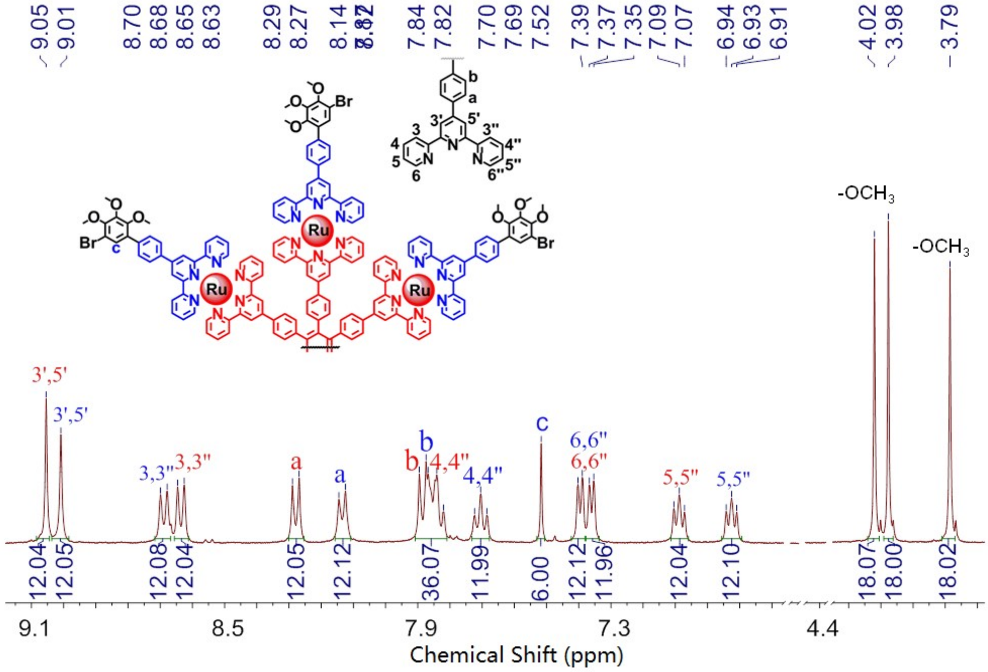


Figure S5. ^{1}H NMR spectrum of compound **4** in CD_3CN.

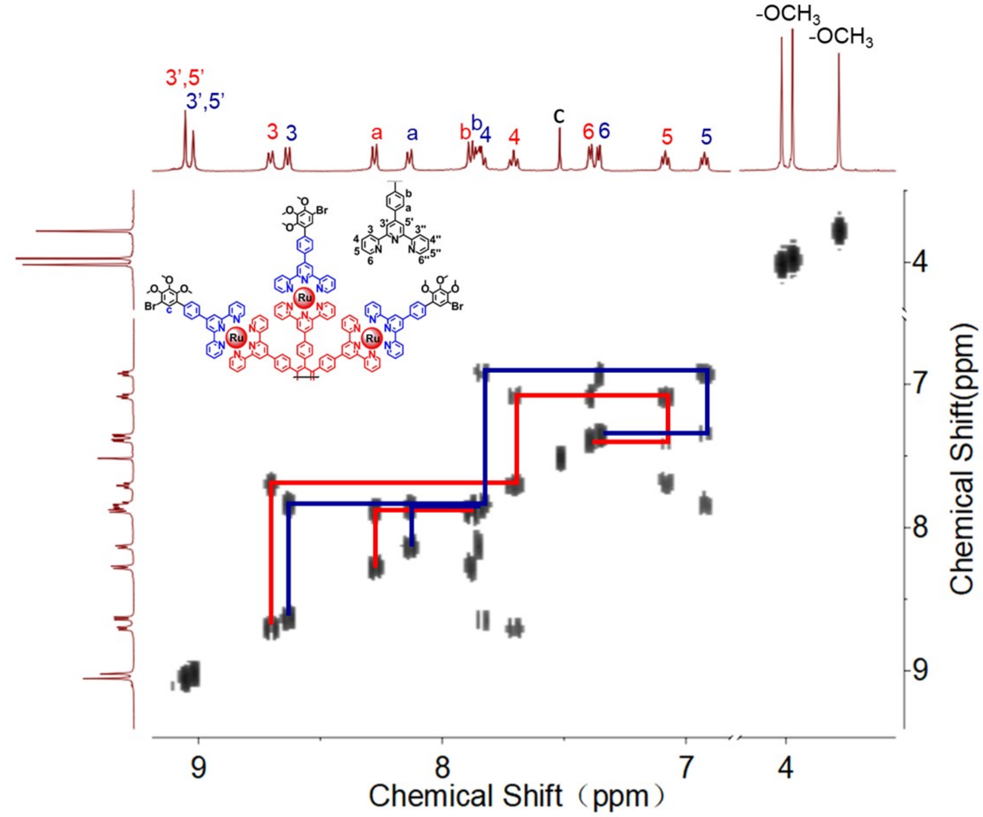


Figure S6. COSY spectrum of compound **4** in CD_3CN.

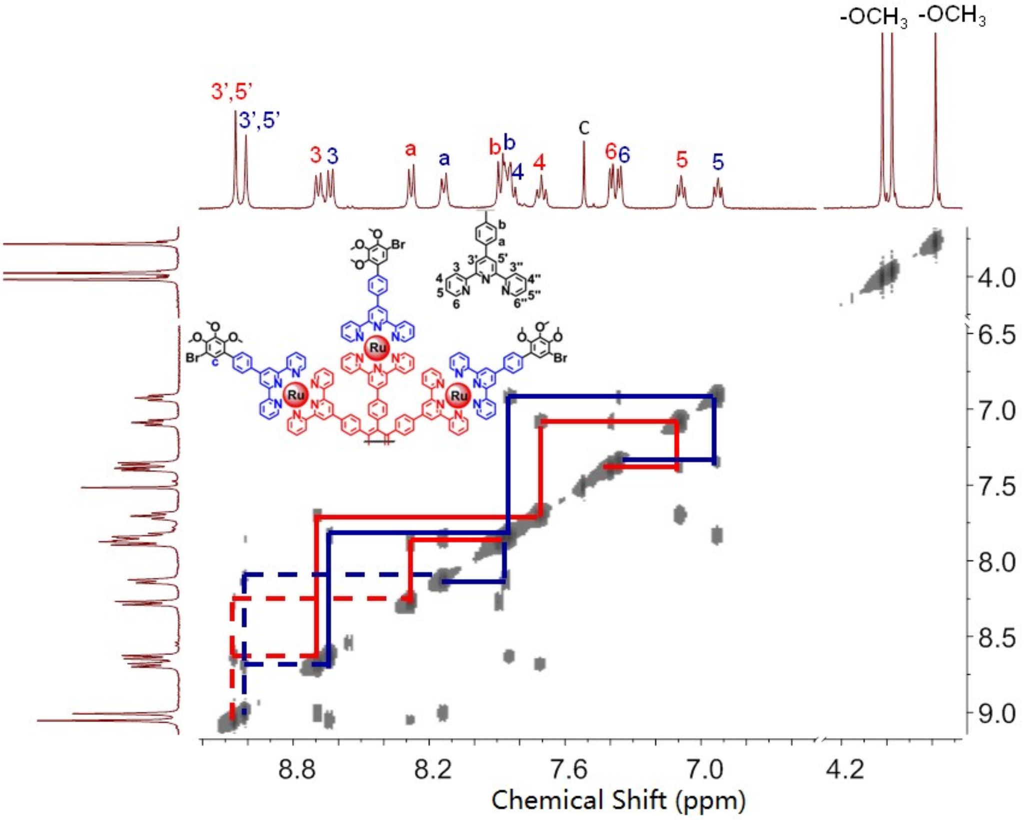


Figure S7. NOESY spectrum of compound **4** in CD$_3$CN.

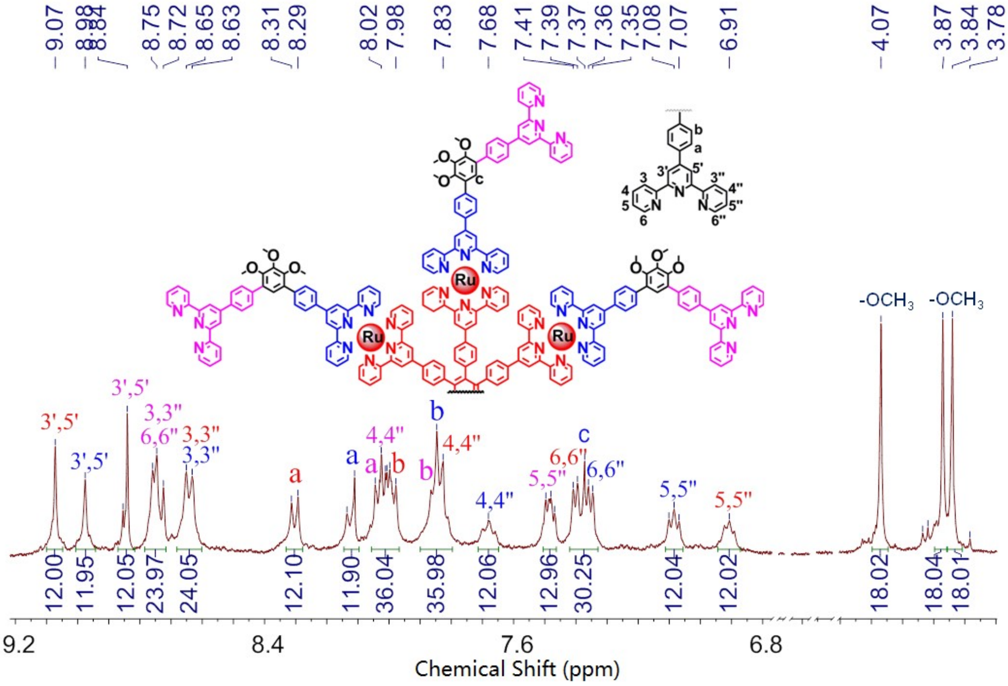


Figure S8. ^{1}H NMR spectrum of compound **L** in CD$_3$CN.

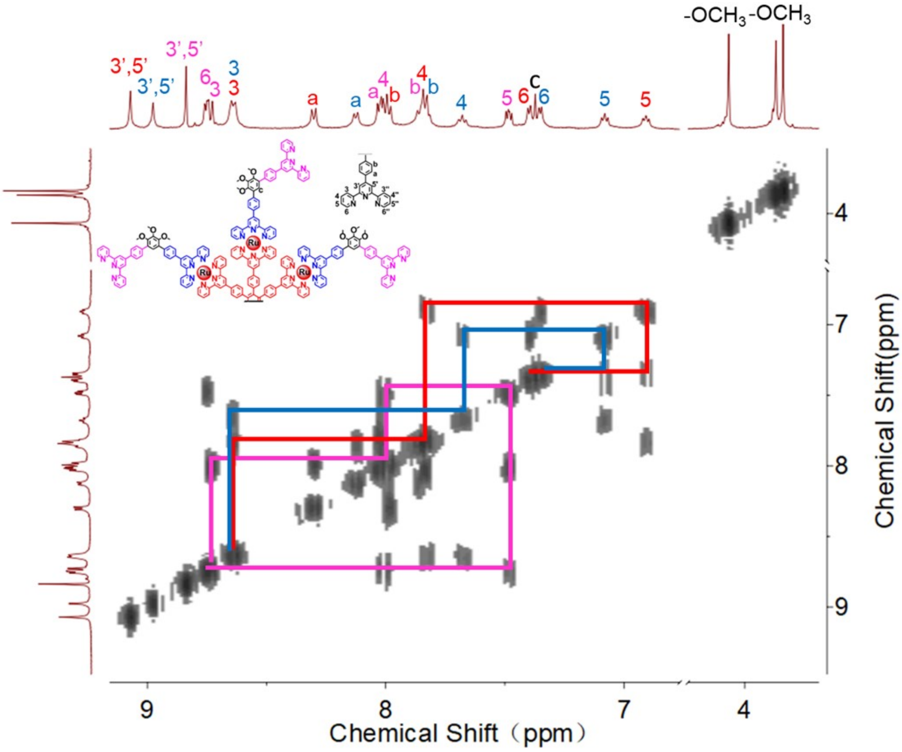


Figure S9. COSY spectrum of compound **L** in CD_3CN.

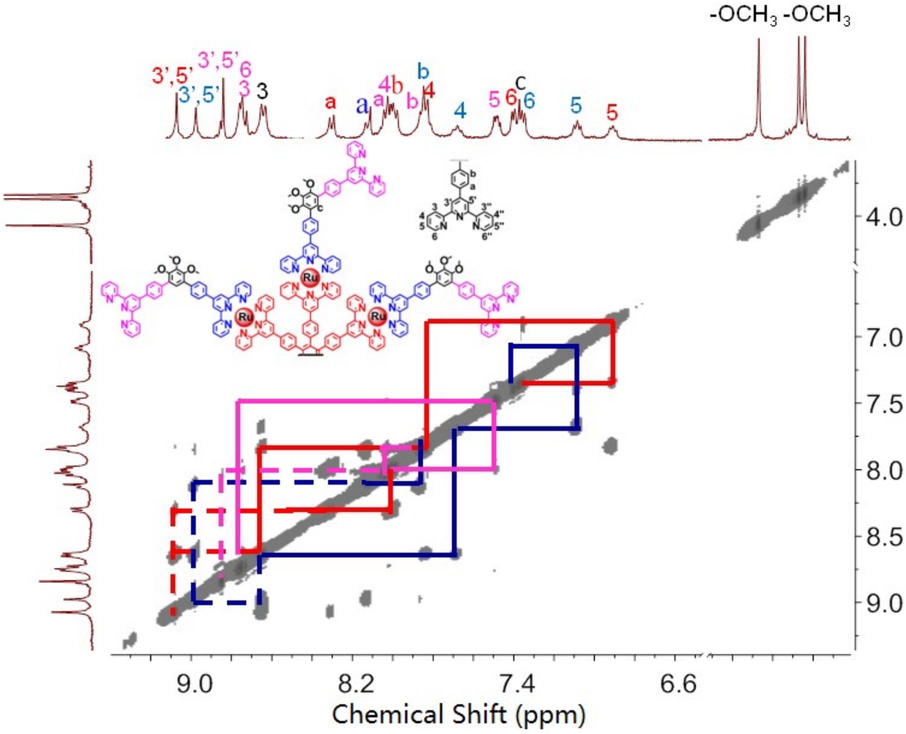


Figure S10. NOESY spectrum of compound **L** in CD_3CN.

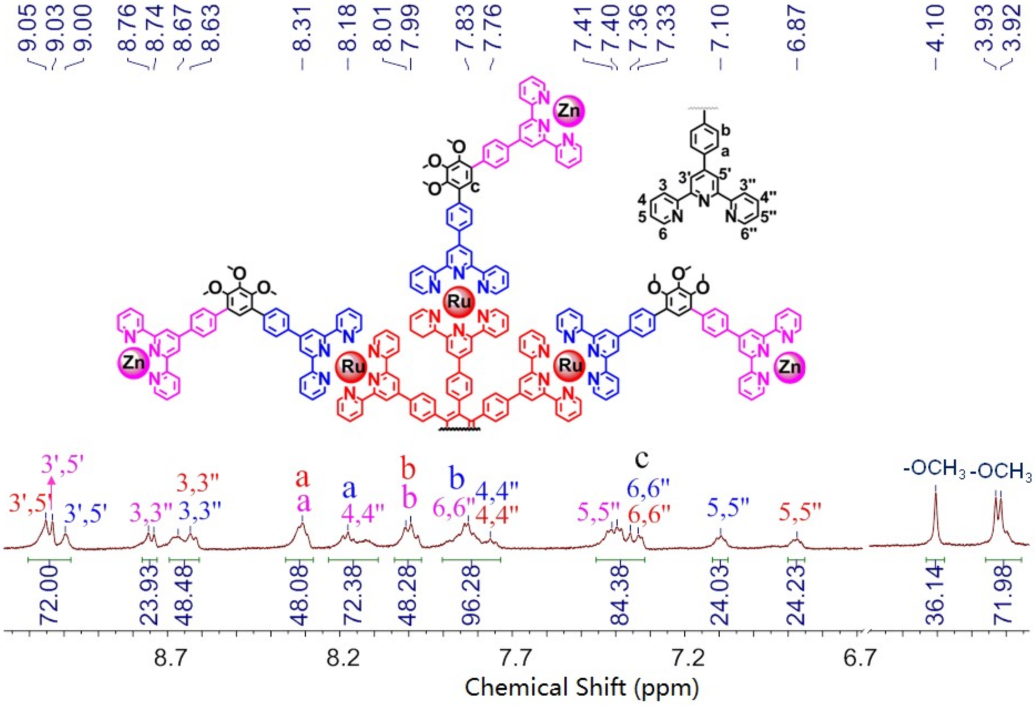


Figure S11. ^{1}H NMR spectrum of **S** in CD_3CN.

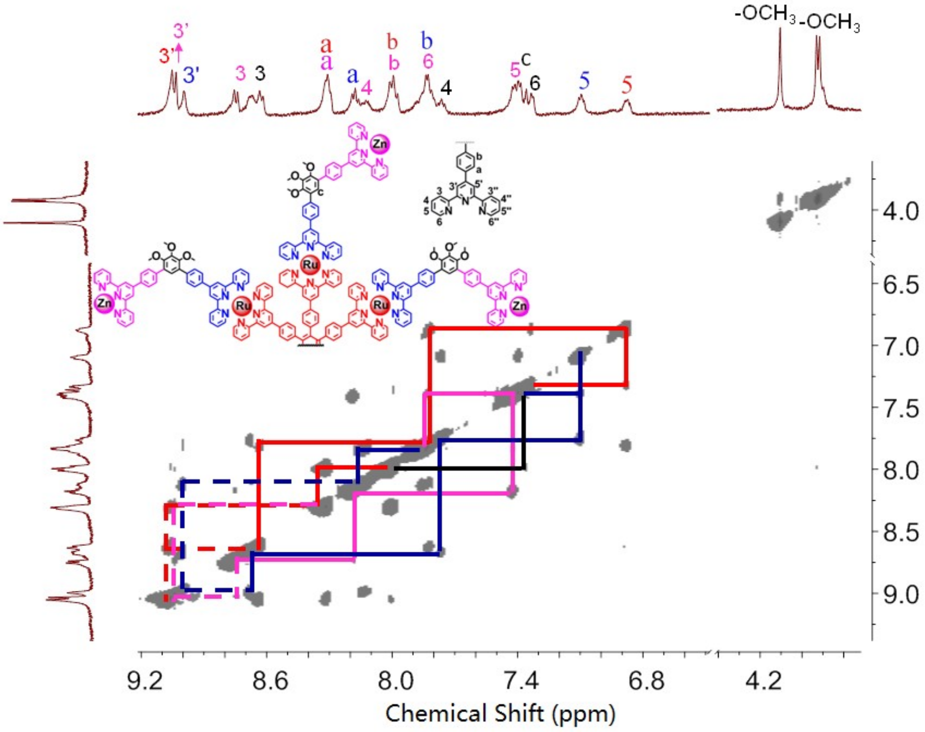


Figure S12. NOESY spectrum of **S** in CD_3CN.

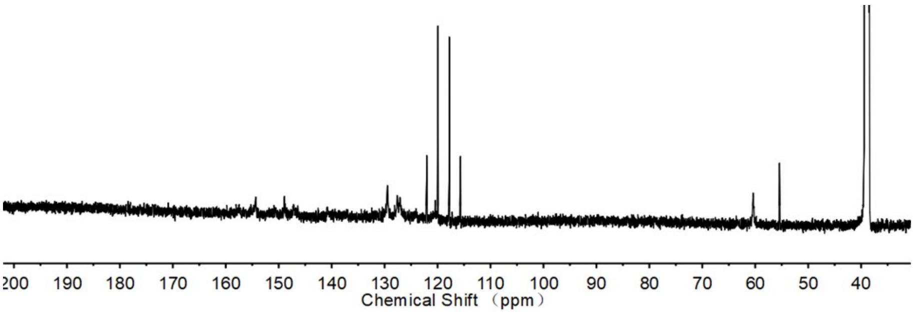


Figure S13: ^{13}C NMR spectrum (600 MHz) of ligand **S** in DMSO-d$_6$.

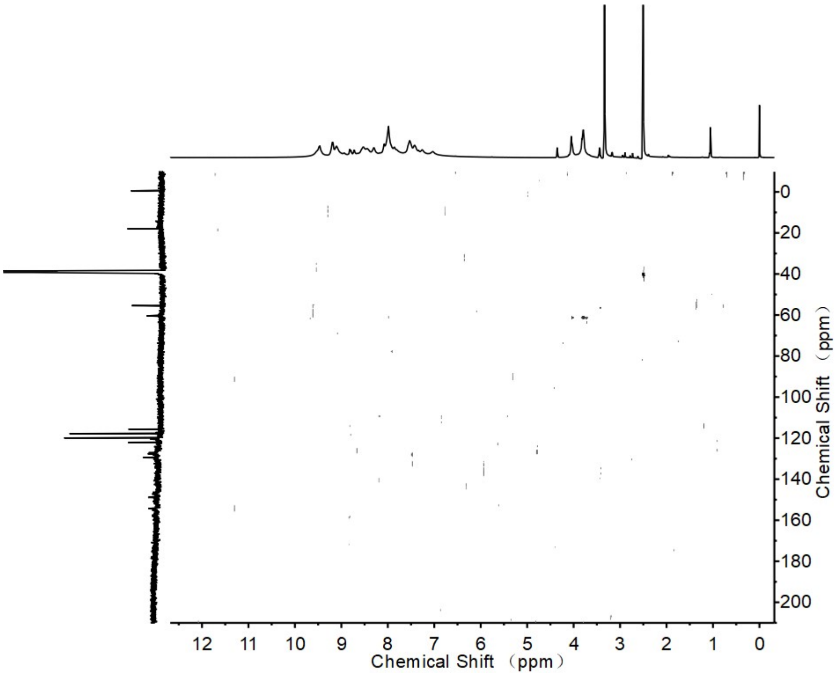


Figure S14: 2D HSQC spectrum (600 MHz) of **S** in DMSO-d$_6$.

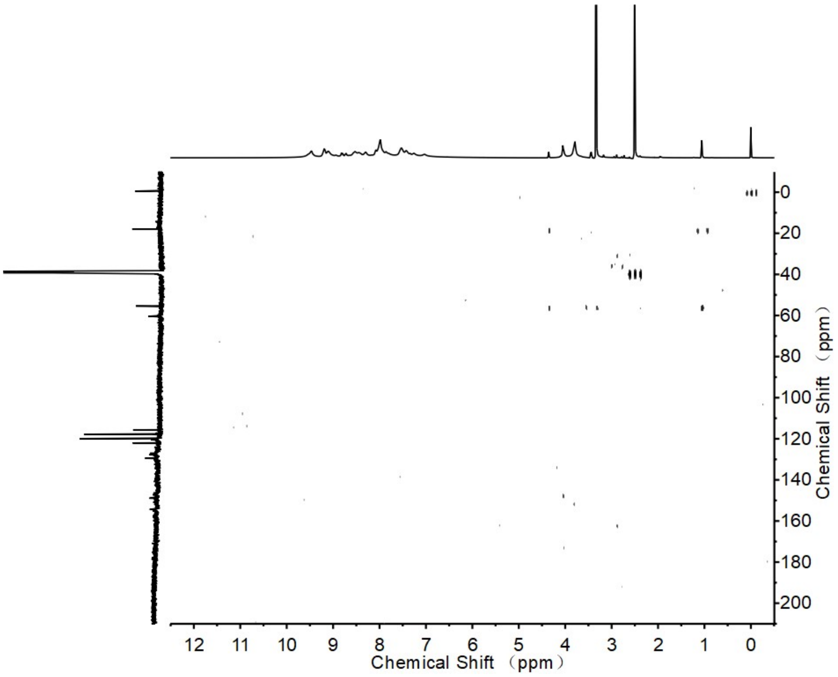


Figure S15: 2D HMBC spectrum (600 MHz) of **L** in DMSO-d_6.

4. ESI-MS spectra of ligands and complexes.

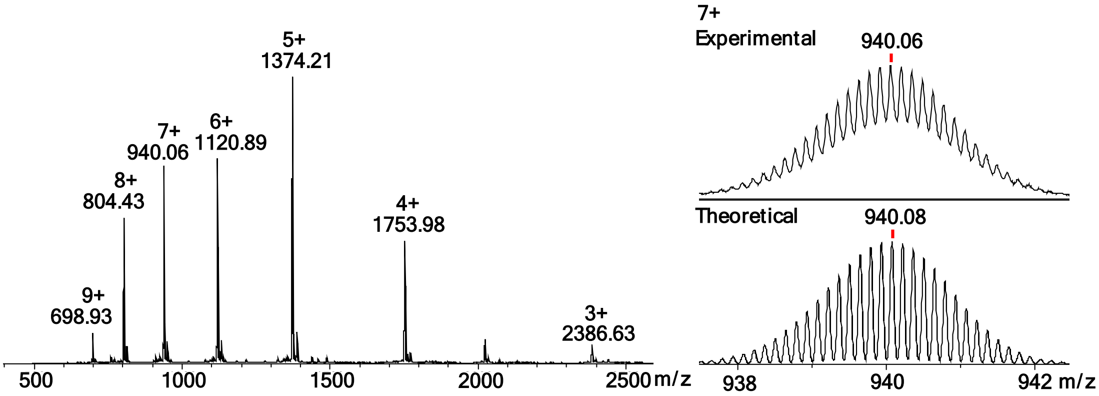


Figure S16. Isotope patterns and ESI-MS spectrum of compound **4**.

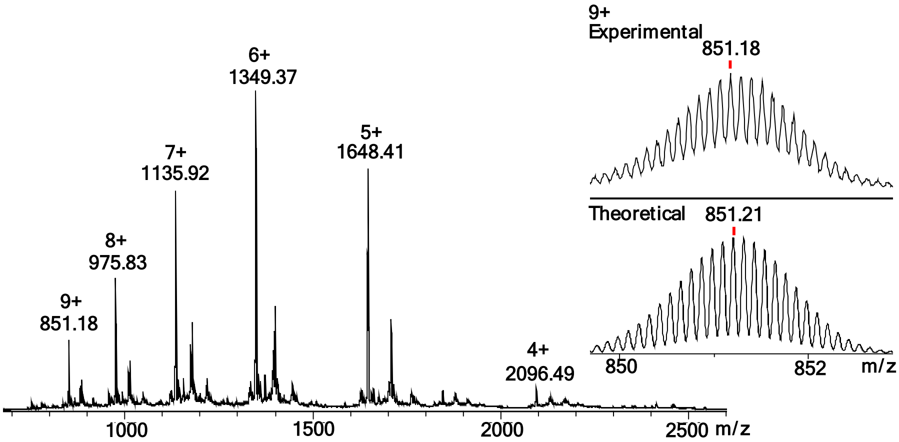


Figure S17. Isotope patterns and ESI-MS spectrum of compound **L**.

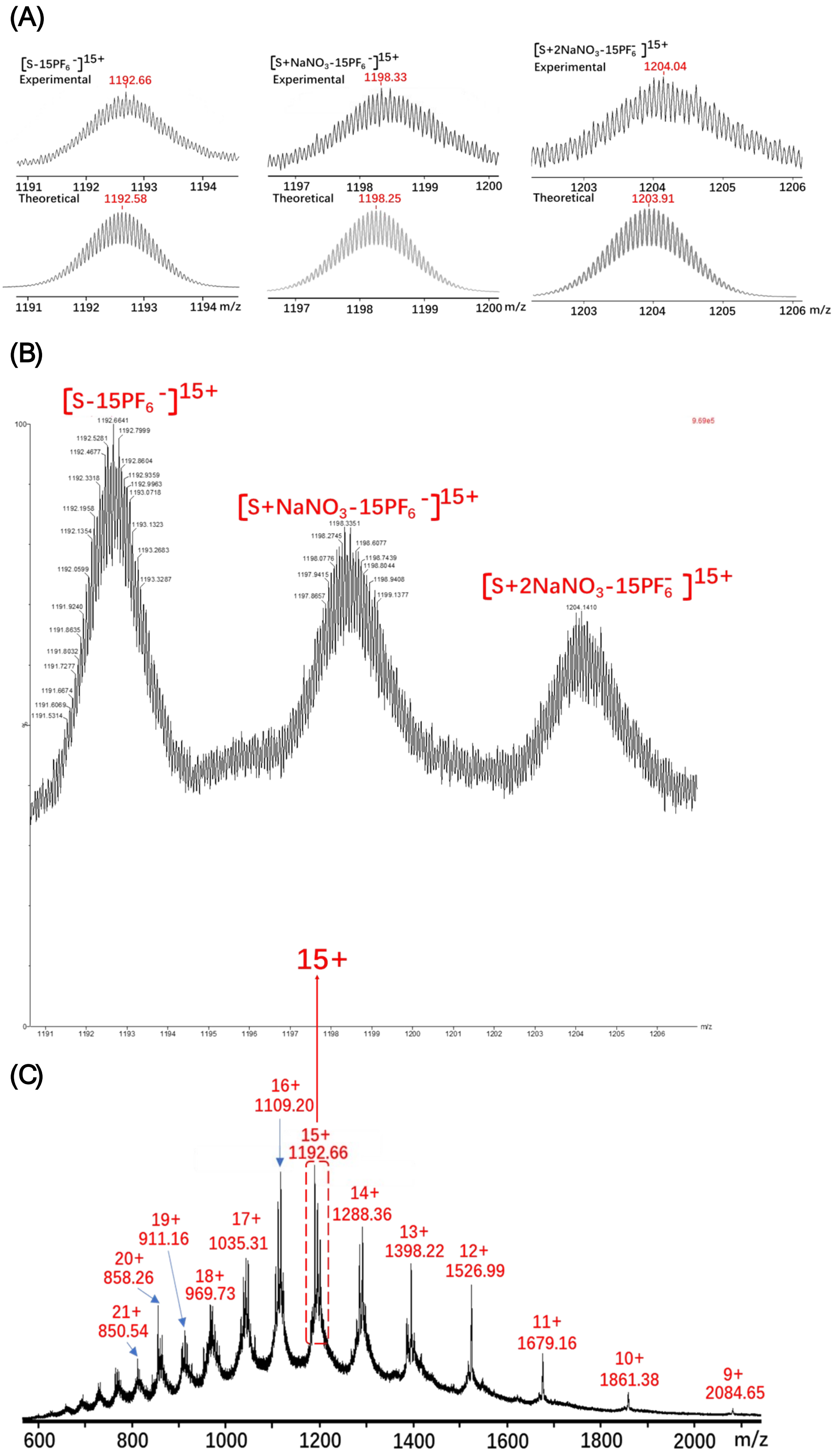
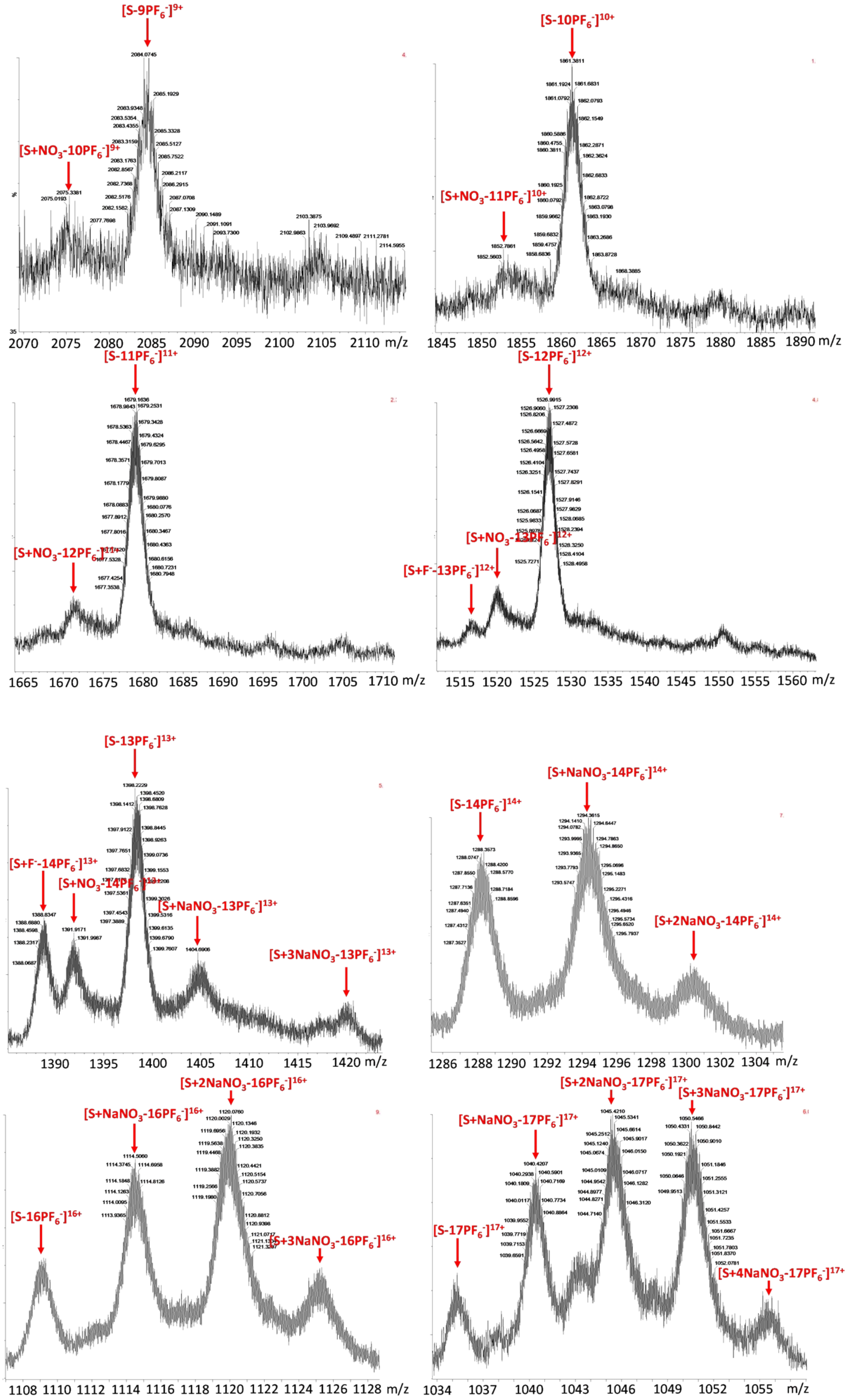


Figure S18. (A) Isotope patterns of [**S**-15PF$_6^-$]$^{15+}$, [**S**+NaNO$_3$-15PF$_6^-$]$^{15+}$ and [**S**+2NaNO$_3$-15PF$_6^-$]$^{15+}$. (B) Enlarged ESI−MS spectrum of [**S**]$^{15+}$. (C) ESI−MS spectrum of **S**.


[S-9PF$_6^-$]$^{9+}$
[S+NO$_3$-10PF$_6^-$]$^{9+}$
2070 2075 2080 2085 2090 2095 2100 2105 2110 m/z
[S-10PF$_6^-$]$^{10+}$
[S+NO$_3$-11PF$_6^-$]$^{10+}$
1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 m/z
[S-11PF$_6^-$]$^{11+}$
[S+NO$_3$-12PF$_6^-$]$^{11+}$
1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 m/z
[S-12PF$_6^-$]$^{12+}$
[S+NO$_3$-13PF$_6^-$]$^{12+}$
[S+F$^-$-13PF$_6^-$]$^{12+}$
1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 m/z
[S-13PF$_6^-$]$^{13+}$
[S+F$^-$-14PF$_6^-$]$^{13+}$
[S+NO$_3$-14PF$_6^-$]$^{13+}$
[S+NaNO$_3$-13PF$_6^-$]$^{13+}$
[S+3NaNO$_3$-13PF$_6^-$]$^{13+}$
1390 1395 1400 1405 1410 1415 1420 m/z
[S+NaNO$_3$-14PF$_6^-$]$^{14+}$
[S-14PF$_6^-$]$^{14+}$
[S+2NaNO$_3$-14PF$_6^-$]$^{14+}$
1286 1288 1290 1292 1294 1296 1298 1300 1302 1304 m/z
[S+2NaNO$_3$-16PF$_6^-$]$^{16+}$
[S+NaNO$_3$-16PF$_6^-$]$^{16+}$
[S-16PF$_6^-$]$^{16+}$
[S+3NaNO$_3$-16PF$_6^-$]$^{16+}$
1108 1110 1112 1114 1116 1118 1120 1122 1124 1126 1128 m/z
[S+2NaNO$_3$-17PF$_6^-$]$^{17+}$
[S+3NaNO$_3$-17PF$_6^-$]$^{17+}$
[S+NaNO$_3$-17PF$_6^-$]$^{17+}$
[S-17PF$_6^-$]$^{17+}$
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1034 1037 1040 1043 1046 1049 1052 1055 m/z

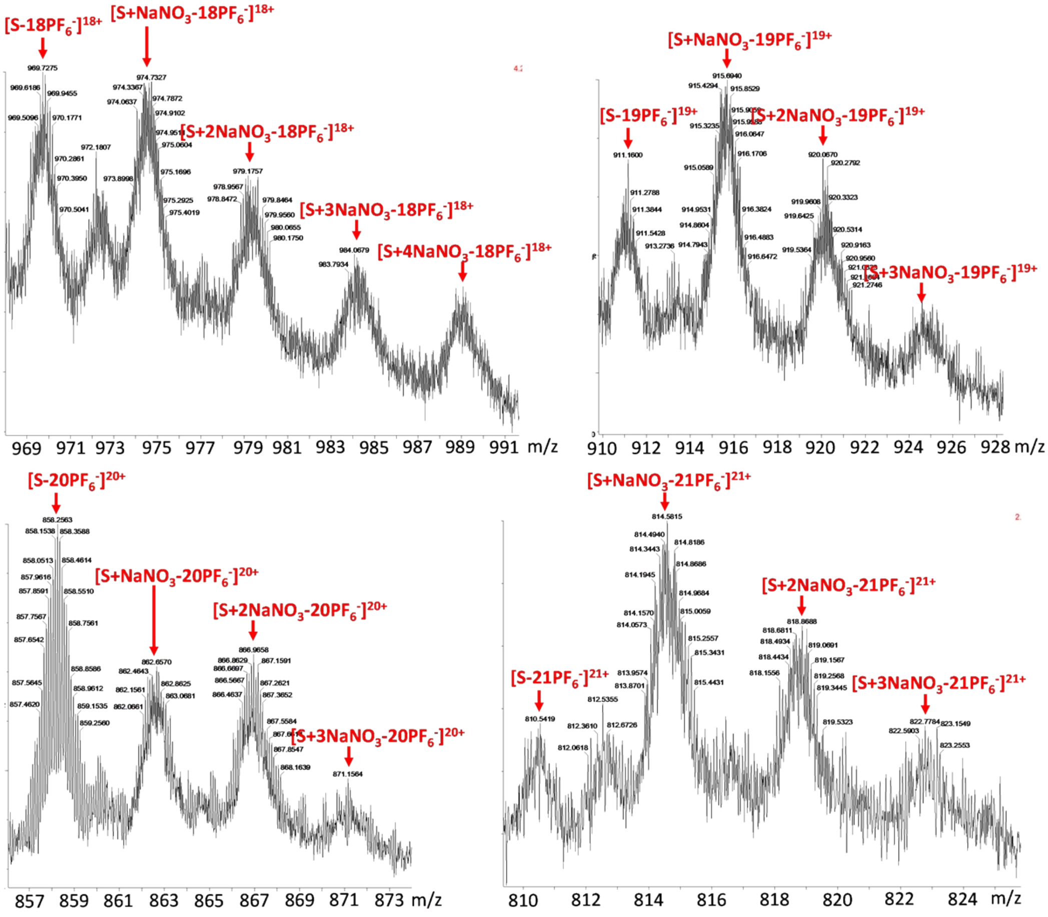
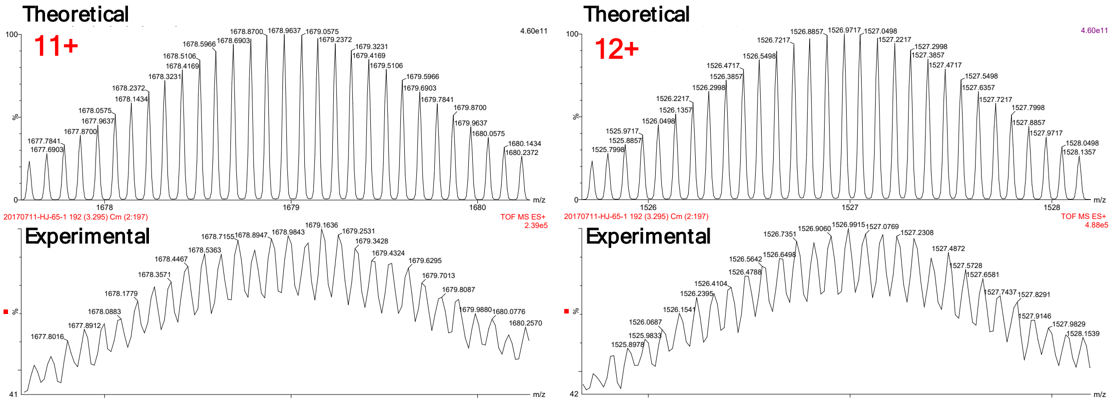


Figure S19. Enlarged view of each charge from 9+ to 21+ and the attribution.



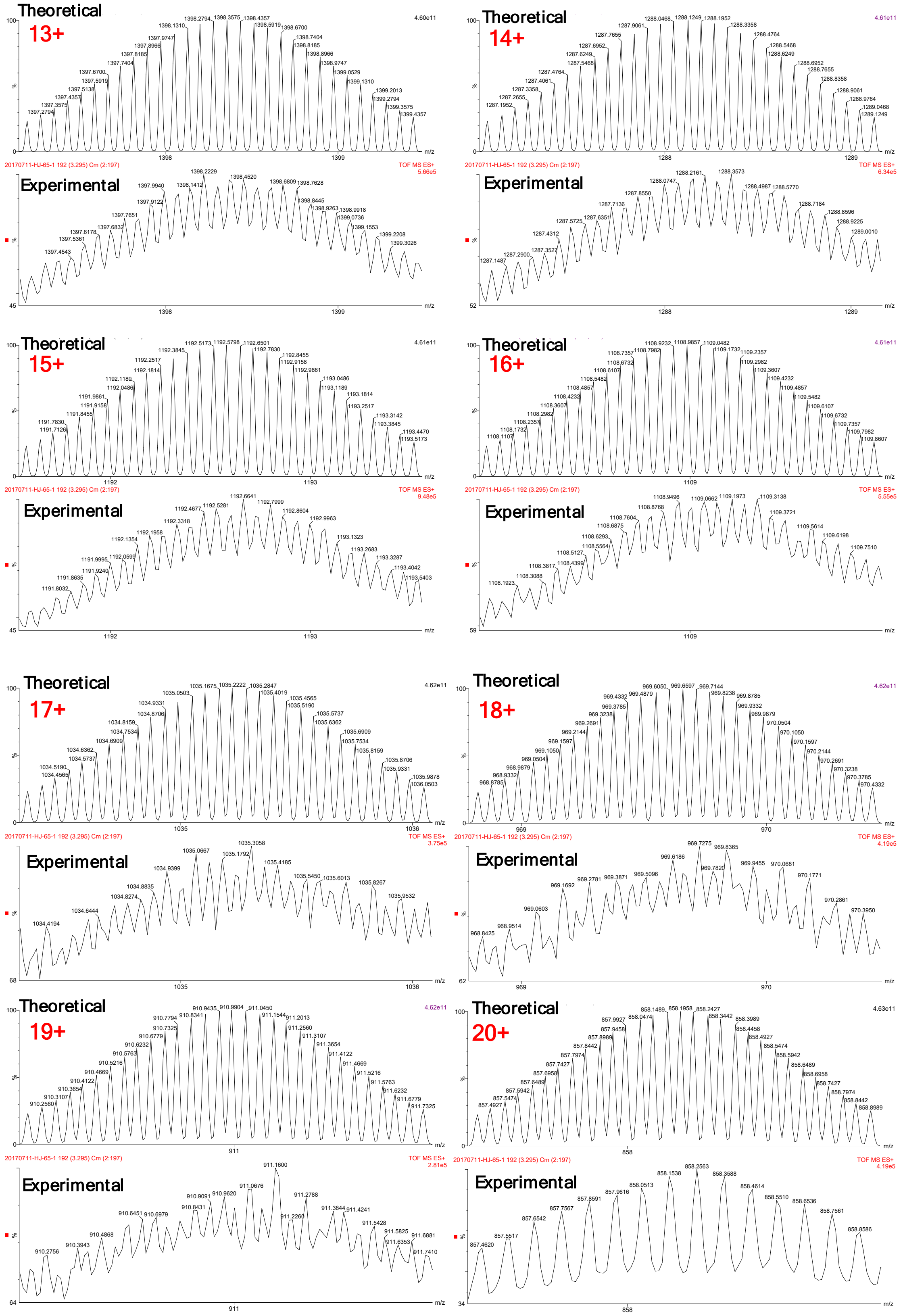


Figure S20. The experimental and theoretical isotope patterns of **S** each charge from 11+ to 20+.

5. TEM and AFM images of S.

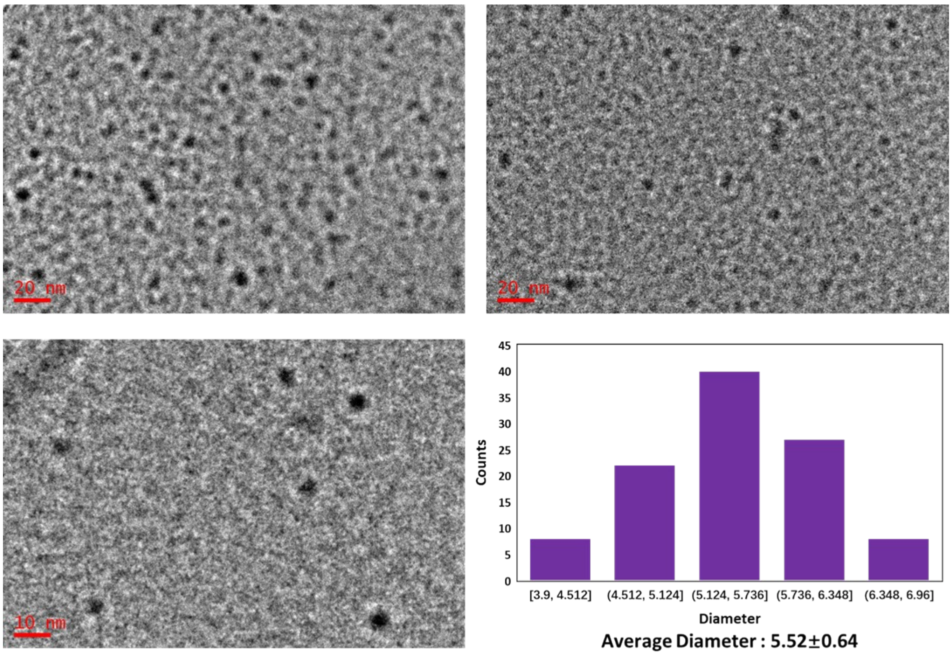


Figure S21. TEM micrograph and statistical size distribution of **S**.

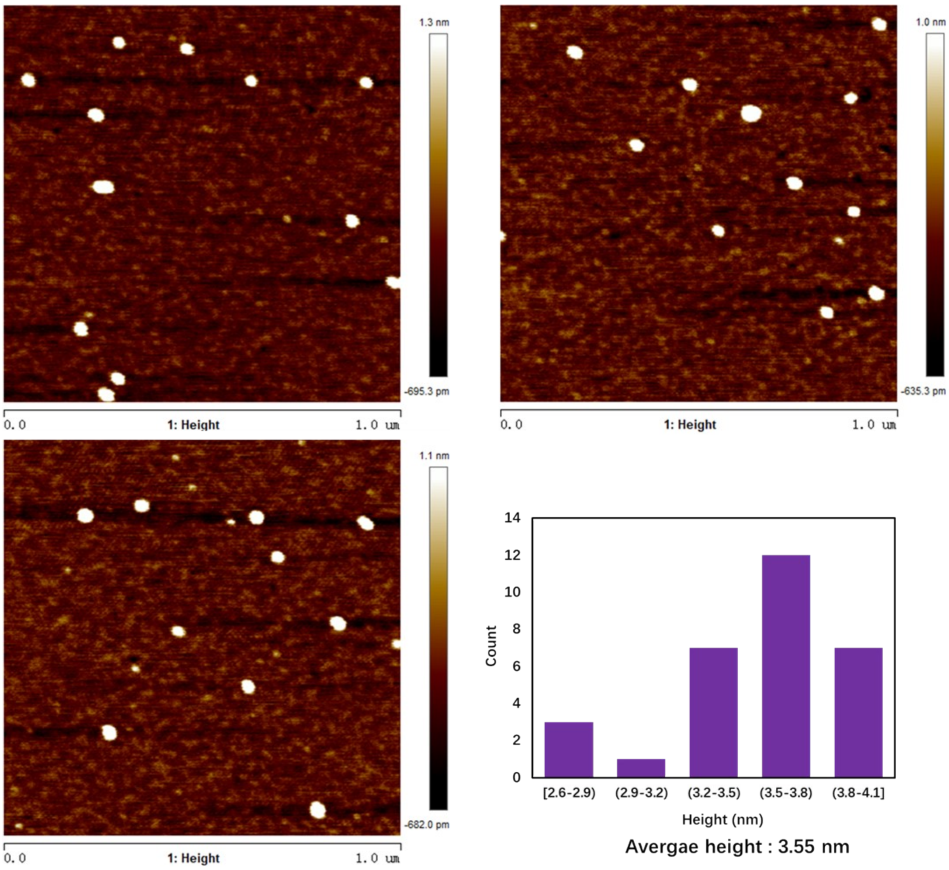


Figure S22. AFM micrograph and statistical size distribution of **S**.

6. Gelation of S and Adsorption of dye molecules by S-G.

The preparation process of **S-G**:

After dissolving **L** (10.0 mg) in 1.0 mL of CH_3CN in a 2.0 mL vial, CH_3OH solution of Zn $(NO_3)_2$ (1.0 mg) was added. The vial was heated at 75 °C for 12 h, then 0.25 mL water was added to the vial. After one day, the solution of **S** will become a **S-G** (Figure S23 A).

The samples of mixture of dyes and complex **S** for NMR experiments:

For four guest molecules with good solubility in CD_3CN (Crystal Violet, Rhodamine B, p-phenylenediamine and resorcinol), our operation was to add 0.1 mL of 4.0 mg/mL CD_3CN solution of guest molecules into 0.5 mL 4.0 mg/mL **S** CD_3CN solution; For the other three guest molecules with general solubility in CD_3CN (Sulforhodamine B, Metanil Yellow and Methylene Blue), our operation was to add 0.1 mL 2.0 mg/mL CD_3CN solution of guest molecules into 0.5 mL 4.0 mg/mL **S** CD_3CN solution; After shook and heated for 30 min, these solution were characterized by ^1H NMR spectroscopy.

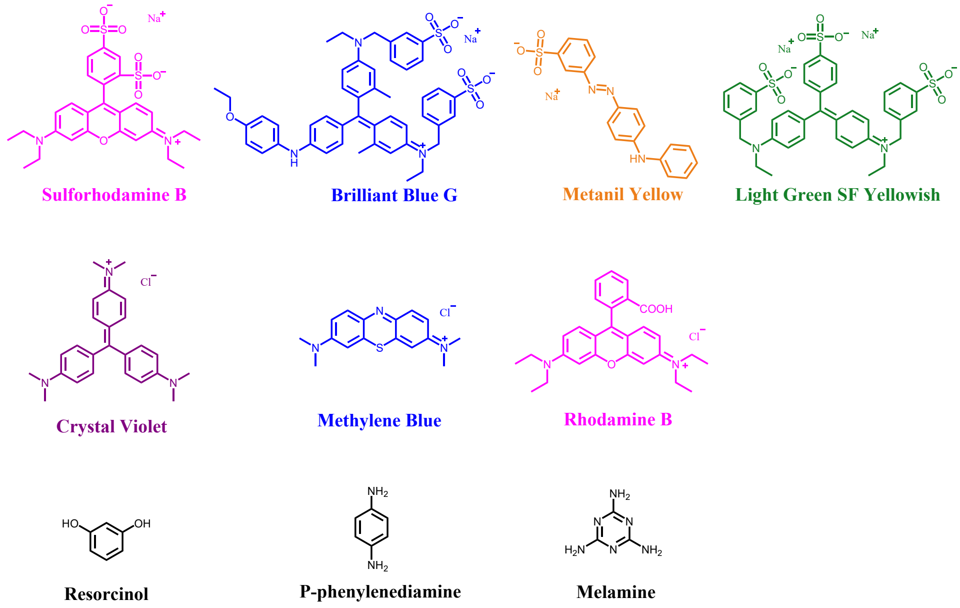
The dye adsorption experiments of powder **S**:

First, adding 1.5 mL Sulforhodamine B aqueous solution (11.0 mg/15 mL) and 6.5 mL H_2O. into a 15 mL vial produced the dyes solution. Then 10.0 mg of **S** powder was added to dyes solution. The mixture was shaken for 5 minutes and placed for 2 days, then afforded to next tests.

The general process of dye adsorption experiments of **S-G**:

The **S-G** (10.0 mg complex **S**) was added into 8.0 mL dye solution (c = 1.1 mg / 8.0 mL). 50.0 uL sample was taken out at different points in time for Uv-vis and Fluorescence tests to monitor the adsorption process.

The saturated adsorption capacity was calculated by determining the dye concentration before and after adsorption. The **S-G** (10.0 mg complex **S**) was added into excess dye solution. After placed for 12 h, 50.0 uL sample was taken out to determine the concentration by Uv-vis spectroscopy.



Scheme S3 Structure of seven dye molecules and three organic molecules.

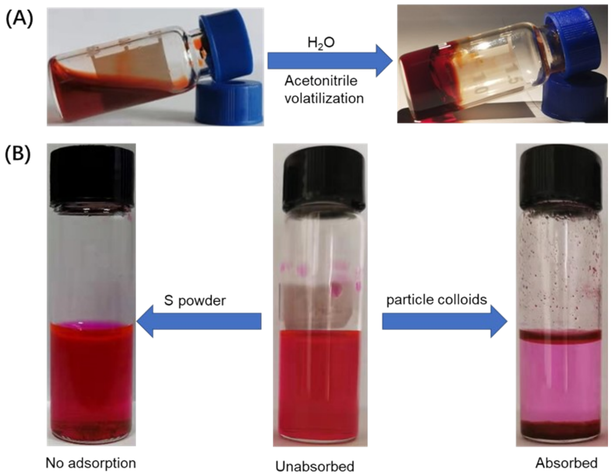


Figure S23. (A) Photographs illustration of **S-G** from CH_3CN solution; (B) The images of SulforhodamineB solution has added **S** powder (left), sulforhodamine B solution (middle) and **S-G** adsorbed sulforhodamine B solution (right).

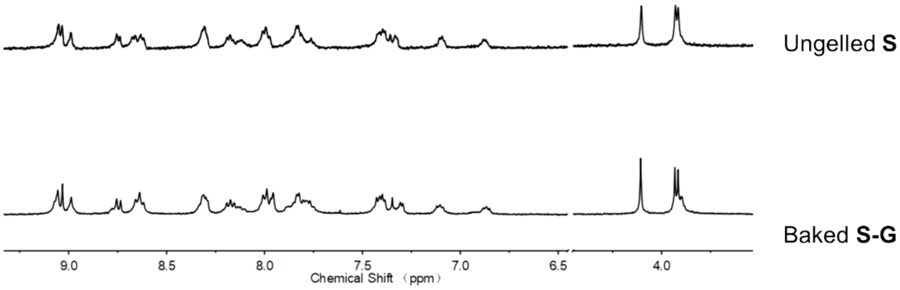


Figure S24. Comparison diagram of ^1H NMR spectrum of Ungelled **S** and Baked **S-G** in CD_3CN.

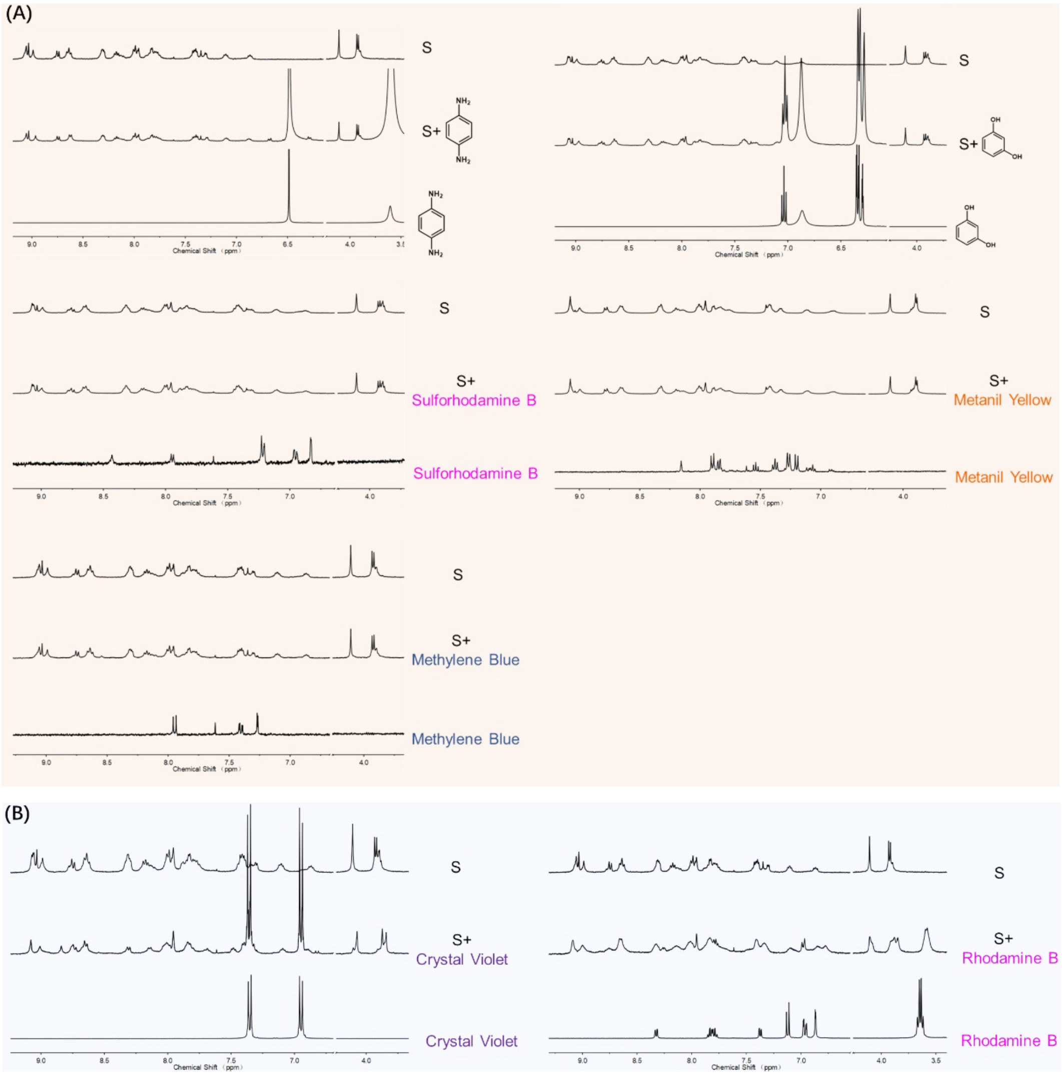


Figure S25. (A) Comparison of ^{1}H NMR spectrum before and after adding P-phenylenediamine, Resorcinol, Sulforhodamine B, Metanil Yellow, Methylene Blue CD_3CN solutions to S's CD_3CN solution; (B) Comparison of ^{1}H NMR spectrum before and after adding Crystal Violet, Rhodamine B CD_3CN solutions to S's CD_3CN solution.

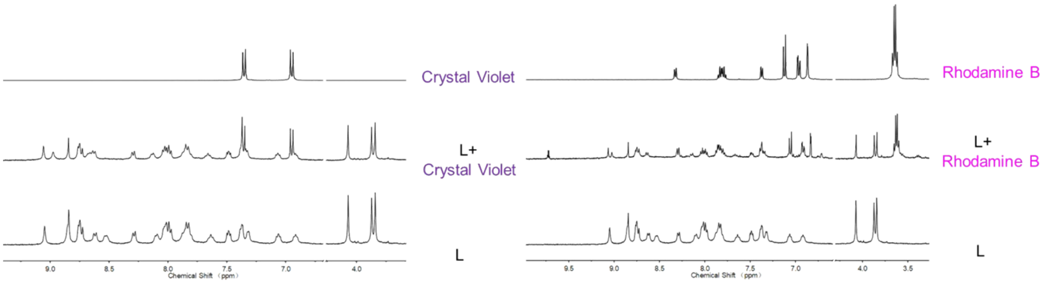


Figure S26. (A) Comparison of 1H NMR spectrum before and after adding Crystal Violet and Rhodamine B to L in CD3CN, respectively.

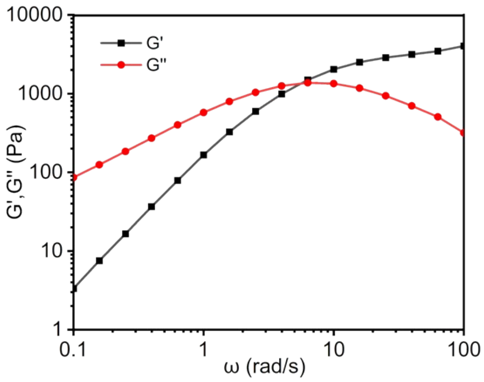


Figure S27. G’ and G’’values of **S-G** on frequency sweep.

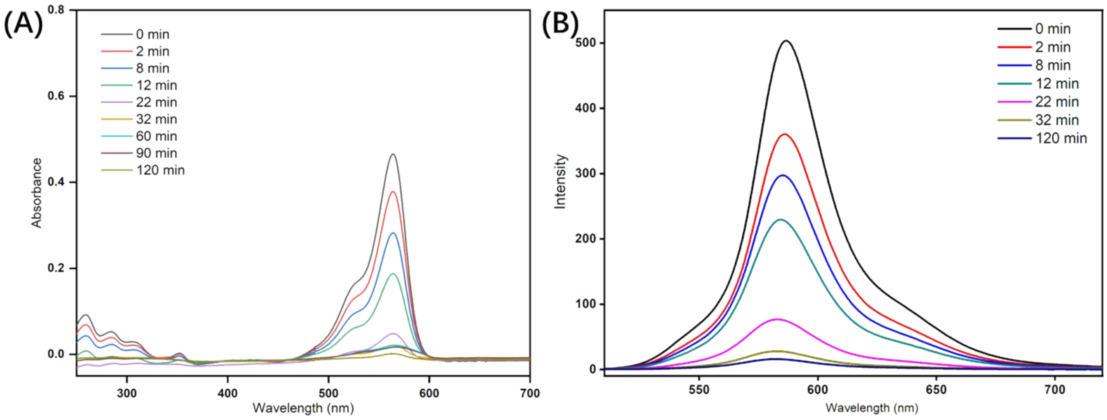


Figure S28. (A) UV spectra of dynamic experiments on **S-G** adsorption of sulforhodamine B at 298K; (B) Fluorescence spectra of dynamic experiments on **S-G** adsorption of sulforhodamine B (λ_{ex} = 563 nm).

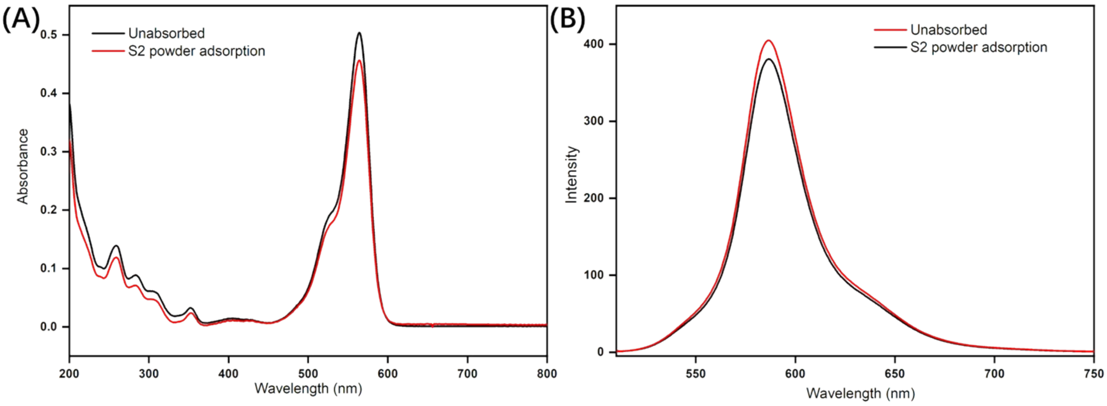
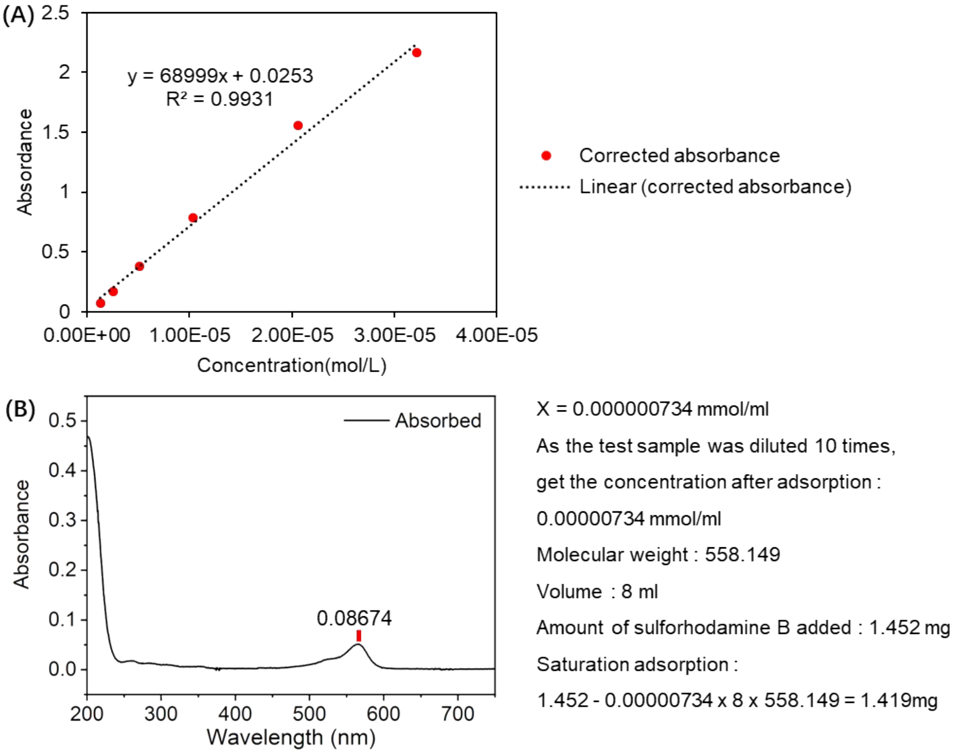


Figure S29. (A) UV spectra of after **S** powder adsorption of sulforhodamine B for 48 h; (B) Fluorescence spectra of after **S** powder adsorption of sulforhodamine B for 48 h.



X = 0.000000734 mmol/ml

As the test sample was diluted 10 times,

get the concentration after adsorption :

0.00000734 mmol/ml

Molecular weight : 558.149

Volume : 8 ml

Amount of sulforhodamine B added : 1.452 mg

Saturation adsorption :

1.452 - 0.00000734 x 8 x 558.149 = 1.419mg

Figure S30. (A) Standard curve of sulforhodamine B concentration and UV absorbance. (B) UV spectrum of excess sulforhodamine B solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

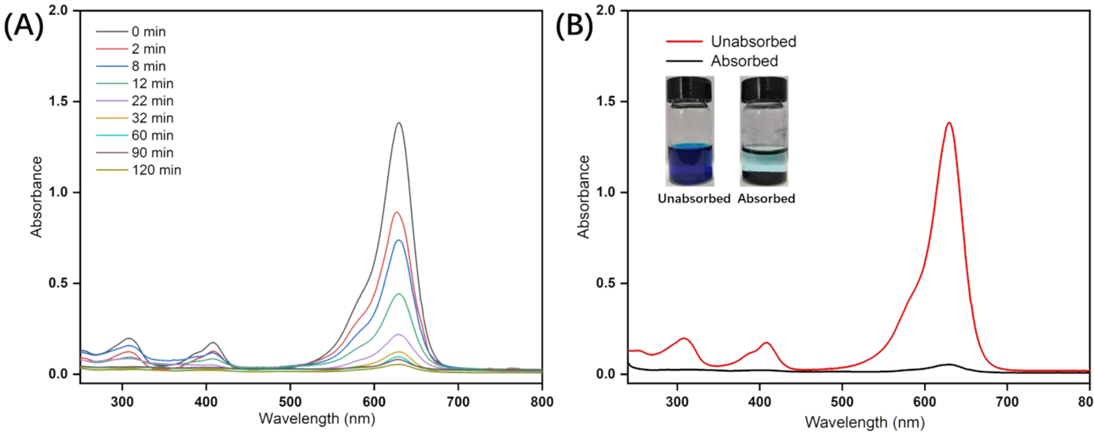
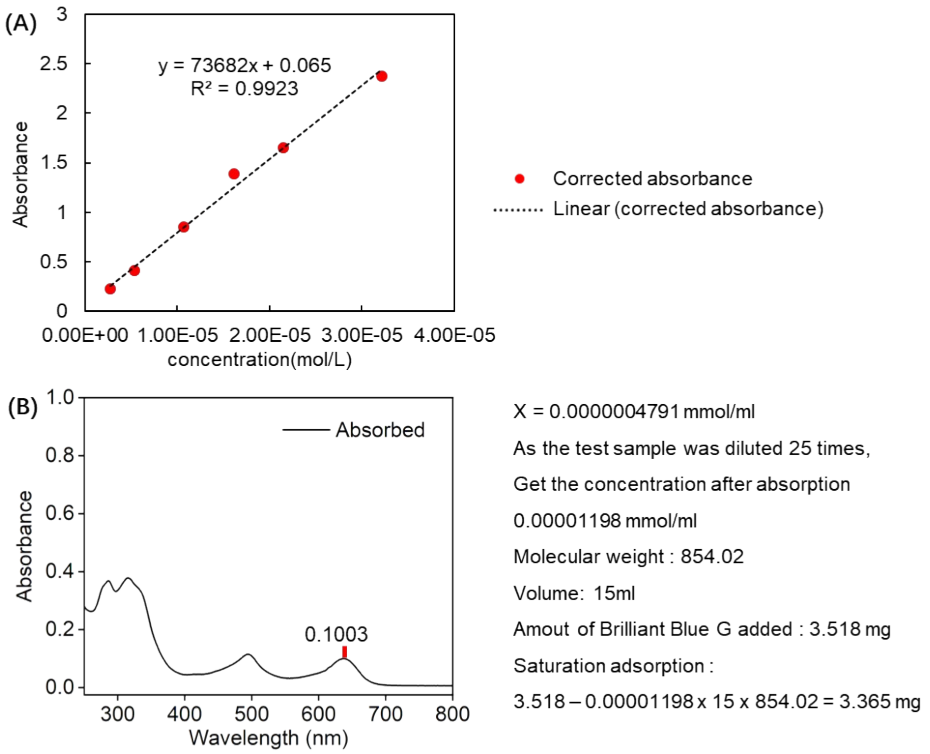


Figure S31. (A) UV spectra of dynamic experiments on **S-G** adsorption of Brilliant Blue G at 298K; (B) UV-vis absorption spectrum of Brilliant Blue G solute before and after adding **S-G** (inset, photographs before and after adsorption).



X = 0.0000004791 mmol/ml

As the test sample was diluted 25 times,

Get the concentration after absorption

0.00001198 mmol/ml

Molecular weight : 854.02

Volume: 15ml

Amout of Brilliant Blue G added : 3.518 mg

Saturation adsorption :

3.518 – 0.00001198 x 15 x 854.02 = 3.365 mg

Figure S32. (A) Standard curve of Brilliant Blue G concentration and UV absorbance. (B) UV spectrum of excess Brilliant Blue G solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

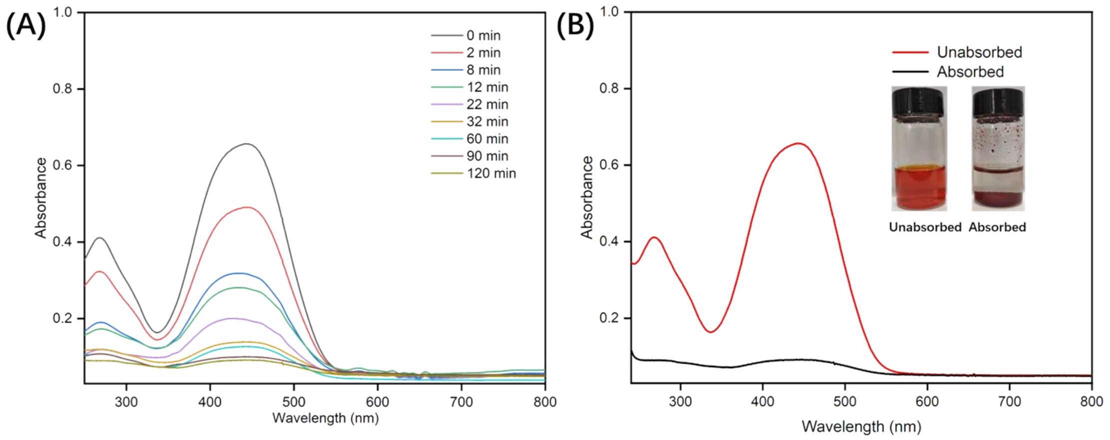
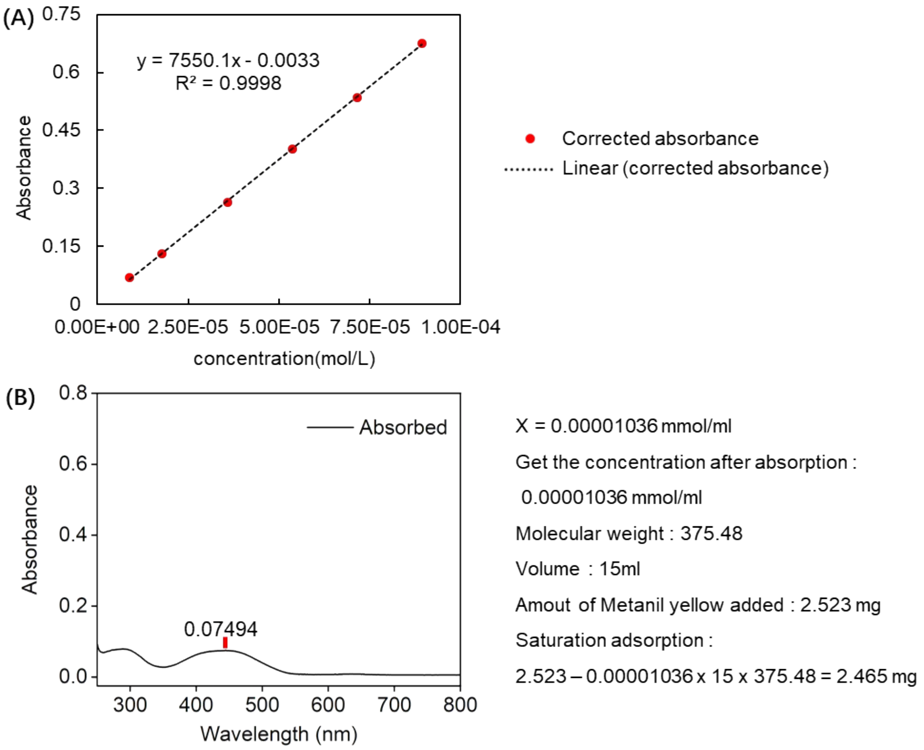


Figure S33. (A) UV spectra of dynamic experiments on **S-G** adsorption of Metanil Yellow at 298K; (B) UV-vis absorption spectrum of Metanil Yellow solute before and after adding **S-G** (inset, photographs before and after adsorption).



X = 0.00001036 mmol/ml

Get the concentration after absorption :

0.00001036 mmol/ml

Molecular weight : 375.48

Volume : 15ml

Amout of Metanil yellow added : 2.523 mg

Saturation adsorption :

2.523 – 0.00001036 x 15 x 375.48 = 2.465 mg

Figure S34. (A) Standard curve of Metanil Yellow concentration and UV absorbance; (B) UV spectrum of excess Metanil Yellow solution adsorbed by 110 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

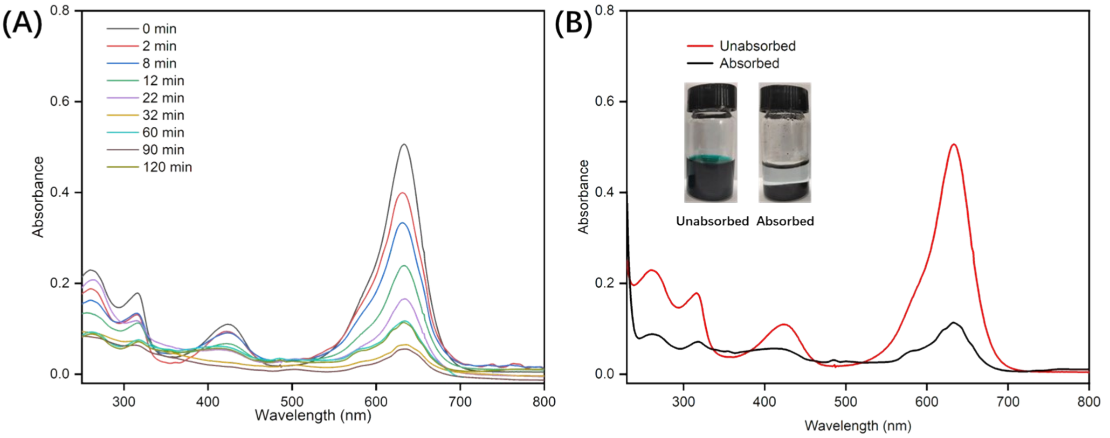
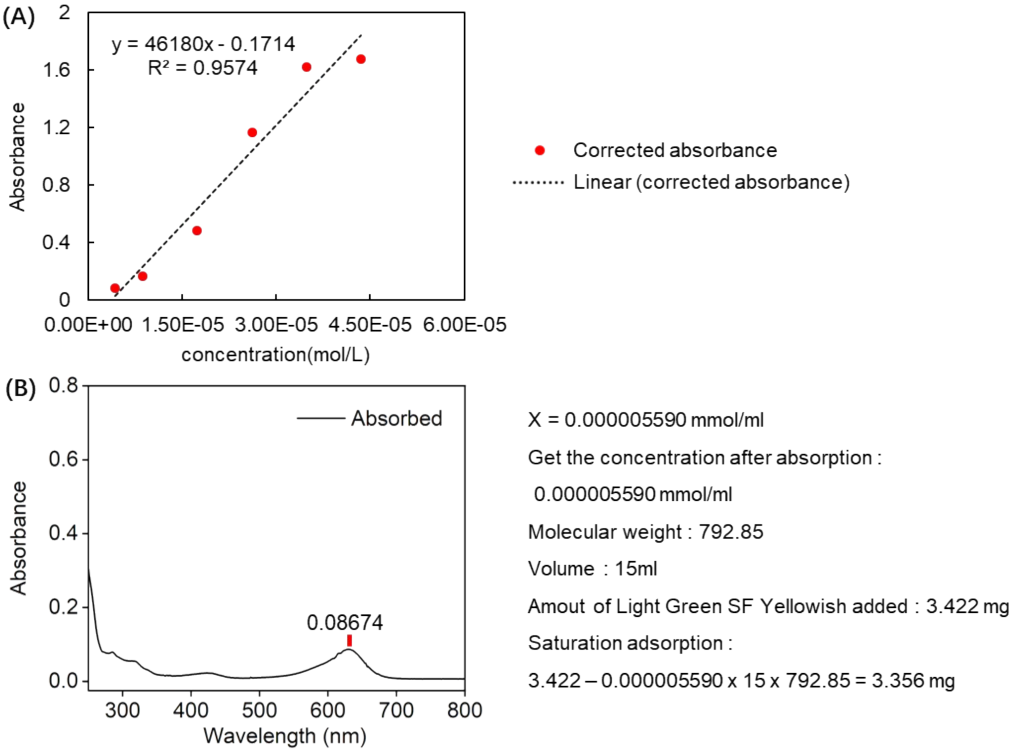


Figure S35. (A) UV spectra of dynamic experiments on **S-G** adsorption of Light Green SF Yellowish at 298K; (B) UV-vis absorption spectrum of Light Green SF Yellowish solute before and after adding **S-G** (inset, photographs before and after adsorption).



X = 0.000005590 mmol/ml

Get the concentration after absorption :

0.000005590 mmol/ml

Molecular weight : 792.85

Volume : 15ml

Amount of Light Green SF Yellowish added : 3.422 mg

Saturation adsorption :

3.422 – 0.000005590 x 15 x 792.85 = 3.356 mg

Figure S36. (A) Standard curve of Light Green SF Yellowish concentration and UV absorbance. (B) UV spectrum of excess Light Green SF Yellowish solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

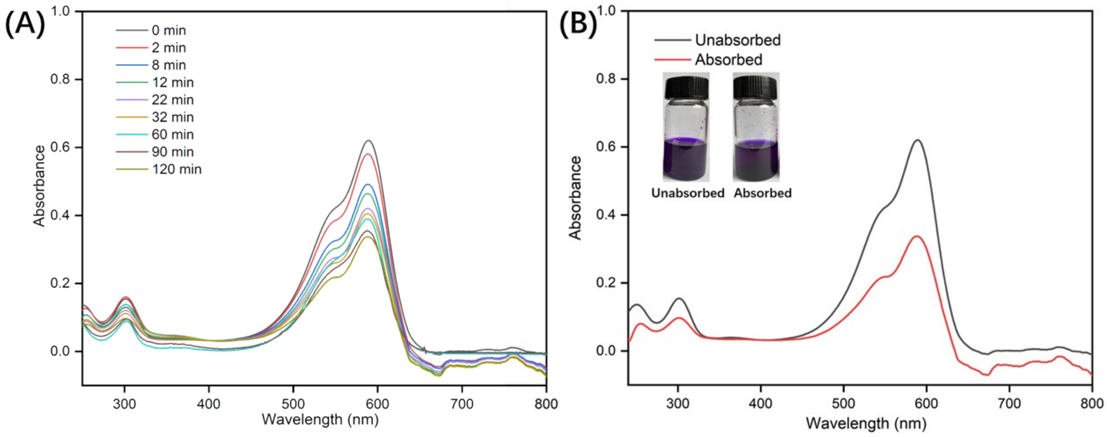
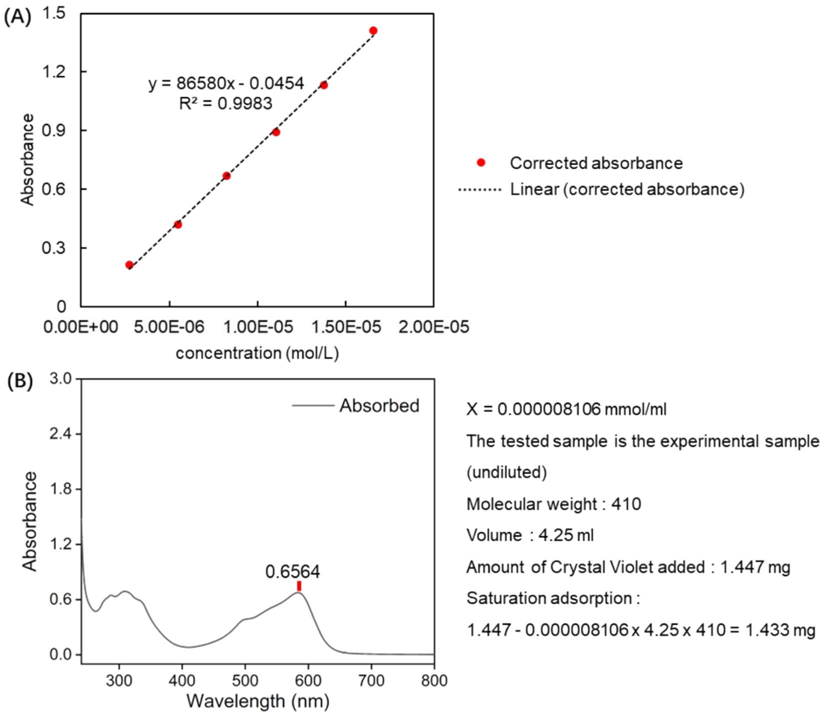


Figure S37. (A) UV spectra of dynamic experiments on **S-G** adsorption of Crystal Violet at 298K; (B) UV-vis absorption spectrum of Crystal Violet solute before and after adding **S-G** (inset, photographs before and after adsorption).



X = 0.000008106 mmol/ml

The tested sample is the experimental sample (undiluted)

Molecular weight : 410

Volume : 4.25 ml

Amount of Crystal Violet added : 1.447 mg

Saturation adsorption :

1.447 - 0.000008106 x 4.25 x 410 = 1.433 mg

Figure S38. (A) Standard curve of Crystal Violet concentration and UV absorbance. (B) UV spectrum of excess Crystal Violet solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

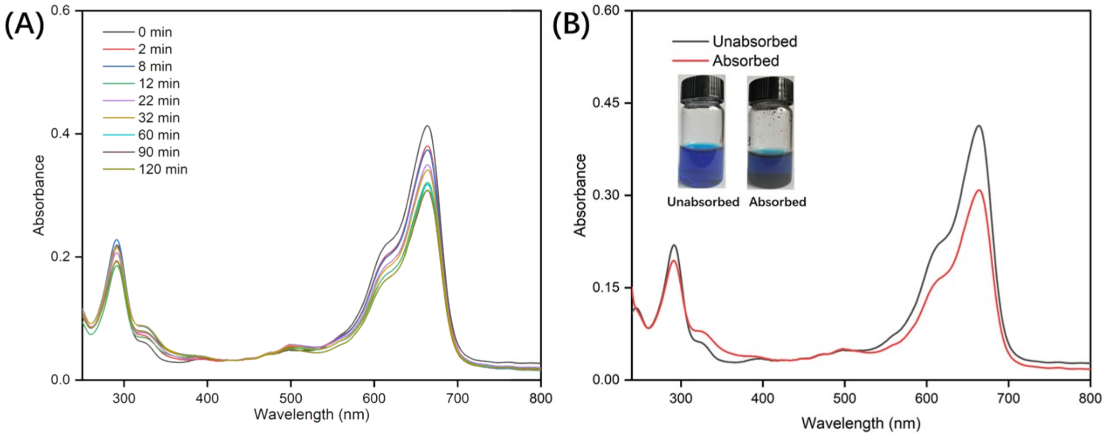
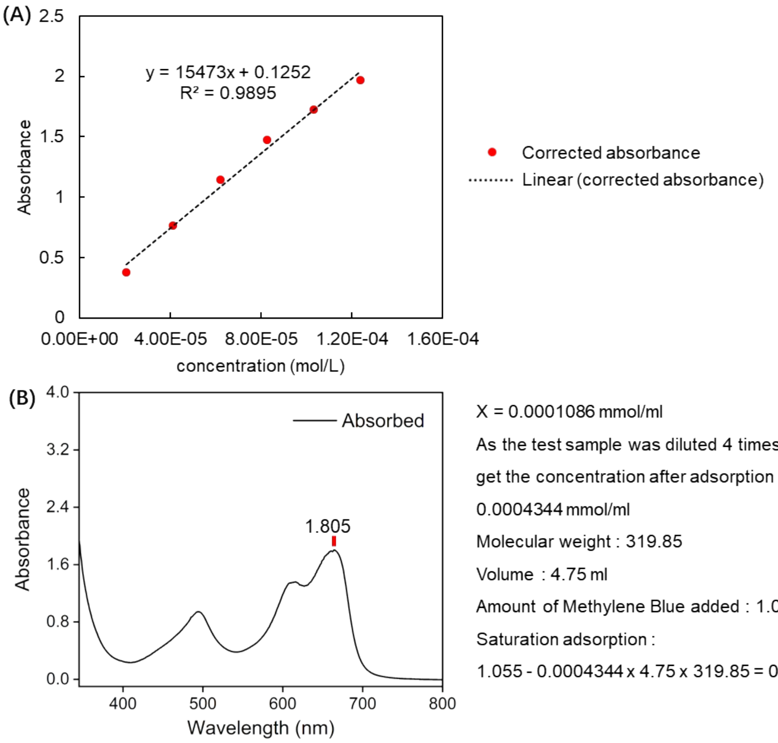


Figure S39. (A) UV spectra of dynamic experiments on **S-G** adsorption of Methylene Blue at 298K; (B) UV-vis absorption spectrum of Methylene Blue solute before and after adding **S-G** (inset, photographs before and after adsorption).



X = 0.0001086 mmol/ml

As the test sample was diluted 4 times,

get the concentration after adsorption :

0.0004344 mmol/ml

Molecular weight : 319.85

Volume : 4.75 ml

Amount of Methylene Blue added : 1.055 mg

Saturation adsorption :

1.055 - 0.0004344 x 4.75 x 319.85 = 0.395 mg

Figure S40. (A) Standard curve of Methylene Blue concentration and UV absorbance. (B) UV spectrum of excess Methylene Blue solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

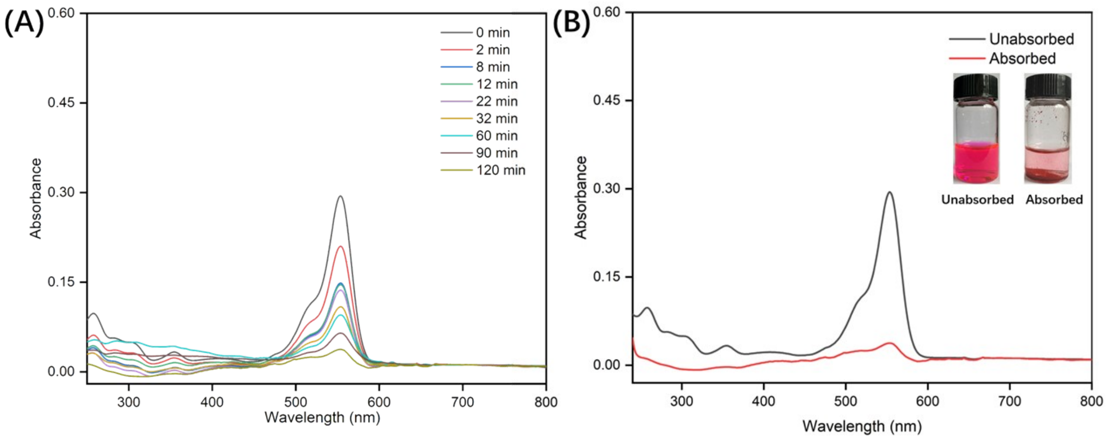
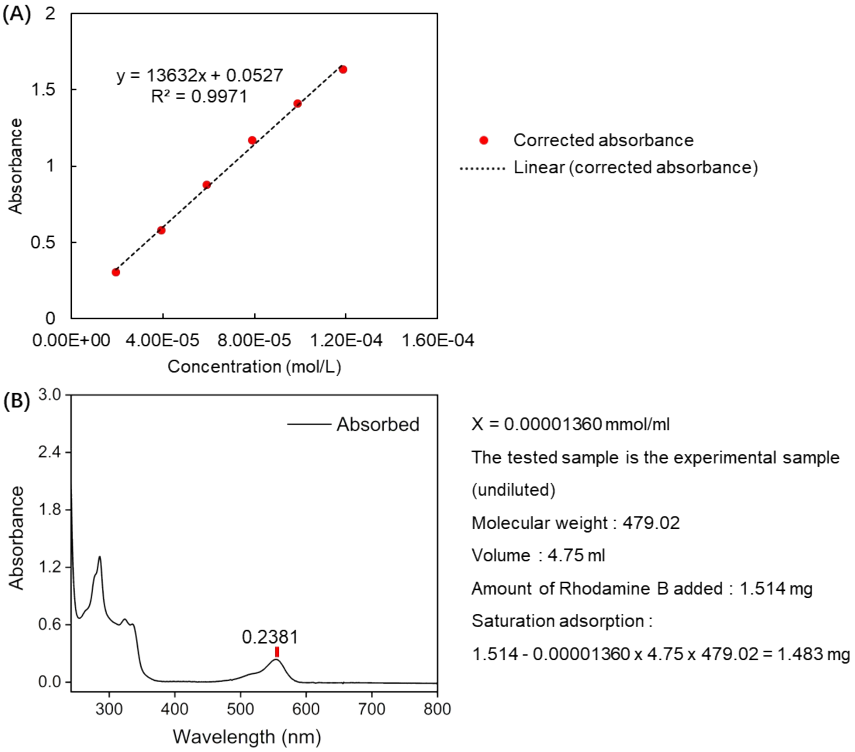


Figure S41. (A) UV spectra of dynamic experiments on **S-G** adsorption of Rhodamine B at 298K; (B) UV-vis absorption spectrum of Rhodamine B solute before and after adding **S-G** (inset, photographs before and after adsorption).



X = 0.00001360 mmol/ml

The tested sample is the experimental sample (undiluted)

Molecular weight : 479.02

Volume : 4.75 ml

Amount of Rhodamine B added : 1.514 mg

Saturation adsorption :

1.514 - 0.00001360 x 4.75 x 479.02 = 1.483 mg

Figure S42. (A) Standard curve of Rhodamine B concentration and UV absorbance. (B) UV spectrum of excess Rhodamine B solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

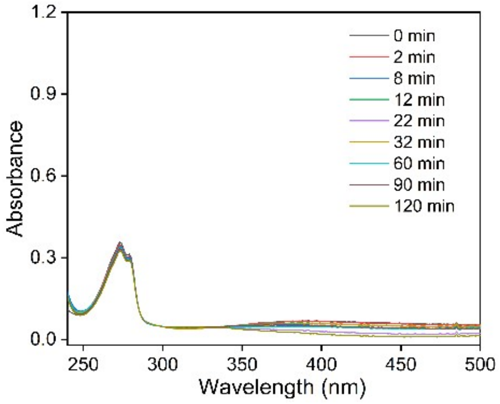
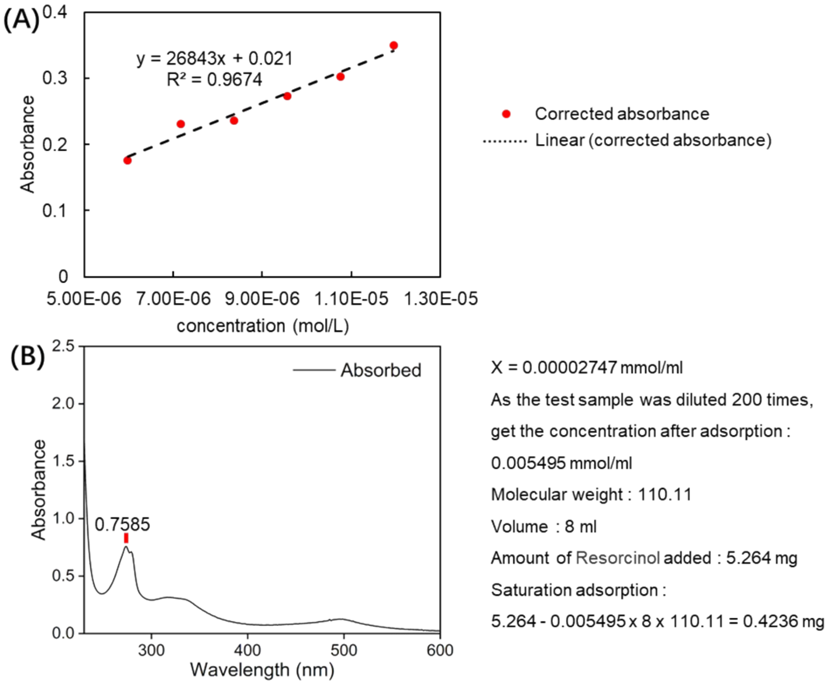


Figure S43. (A) UV spectra of dynamic experiments on **S-G** adsorption of Resorcinol at 298K.



X = 0.00002747 mmol/ml

As the test sample was diluted 200 times,

get the concentration after adsorption :

0.005495 mmol/ml

Molecular weight : 110.11

Volume : 8 ml

Amount of Resorcinol added : 5.264 mg

Saturation adsorption :

5.264 - 0.005495 x 8 x 110.11 = 0.4236 mg

Figure S44. (A) Standard curve of Resorcinol concentration and UV absorbance. (B) UV spectrum of excess Resorcinol solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

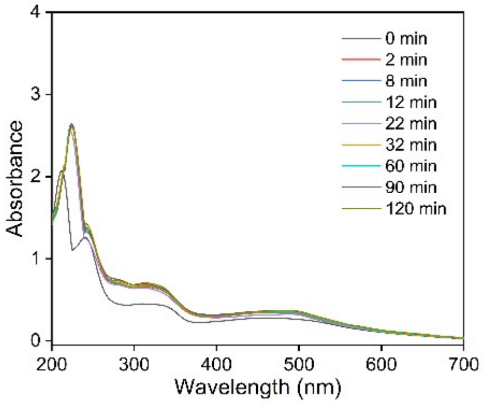
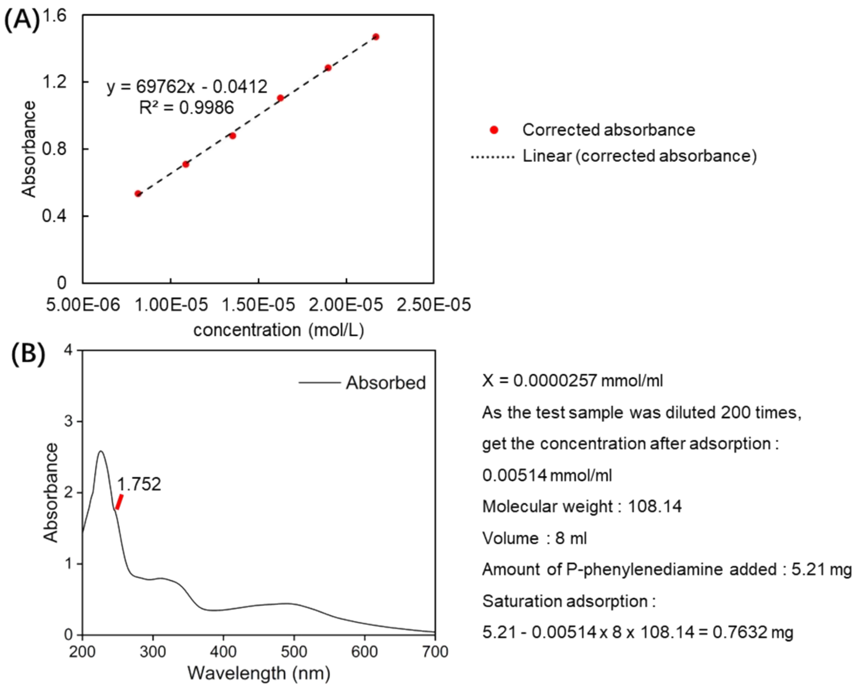


Figure S45. (A) UV spectra of dynamic experiments on **S-G** adsorption of P-phenylenediamine at 298K.



X = 0.0000257 mmol/ml

As the test sample was diluted 200 times,

get the concentration after adsorption :

0.00514 mmol/ml

Molecular weight : 108.14

Volume : 8 ml

Amount of P-phenylenediamine added : 5.21 mg

Saturation adsorption :

5.21 - 0.00514 x 8 x 108.14 = 0.7632 mg

Figure S46. (A) Standard curve of P-phenylenediamine concentration and UV absorbance. (B) UV spectrum of excess P-phenylenediamine solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.

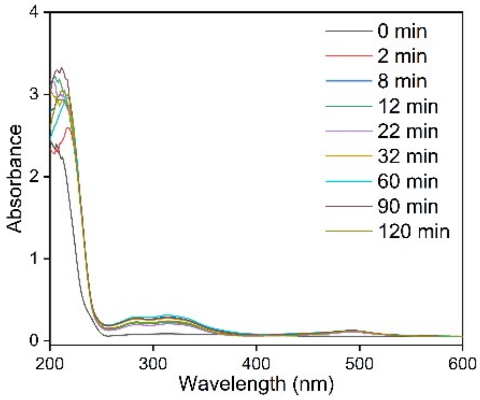
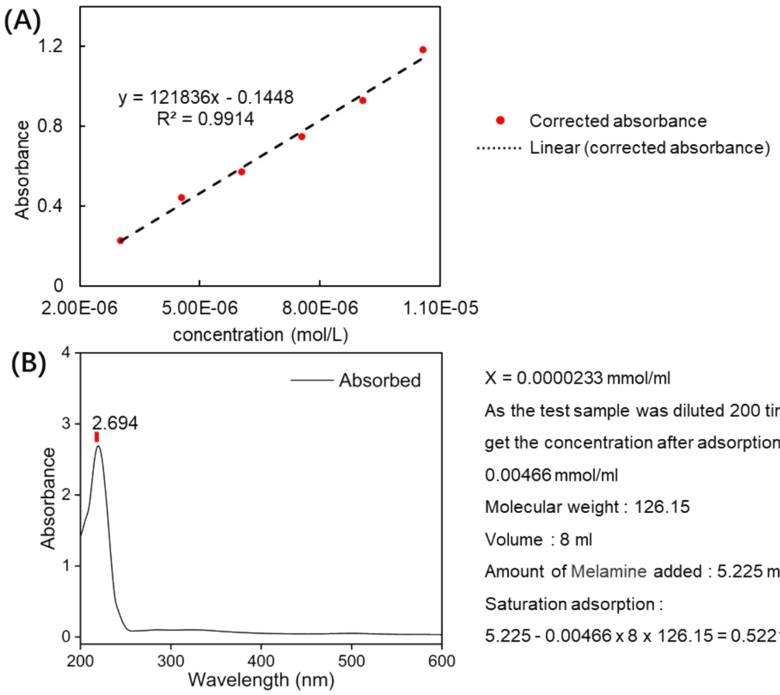


Figure S47. (A) UV spectra of dynamic experiments on **S-G** adsorption of Melamine at 298K.



X = 0.0000233 mmol/ml

As the test sample was diluted 200 times,

get the concentration after adsorption :

0.00466 mmol/ml

Molecular weight : 126.15

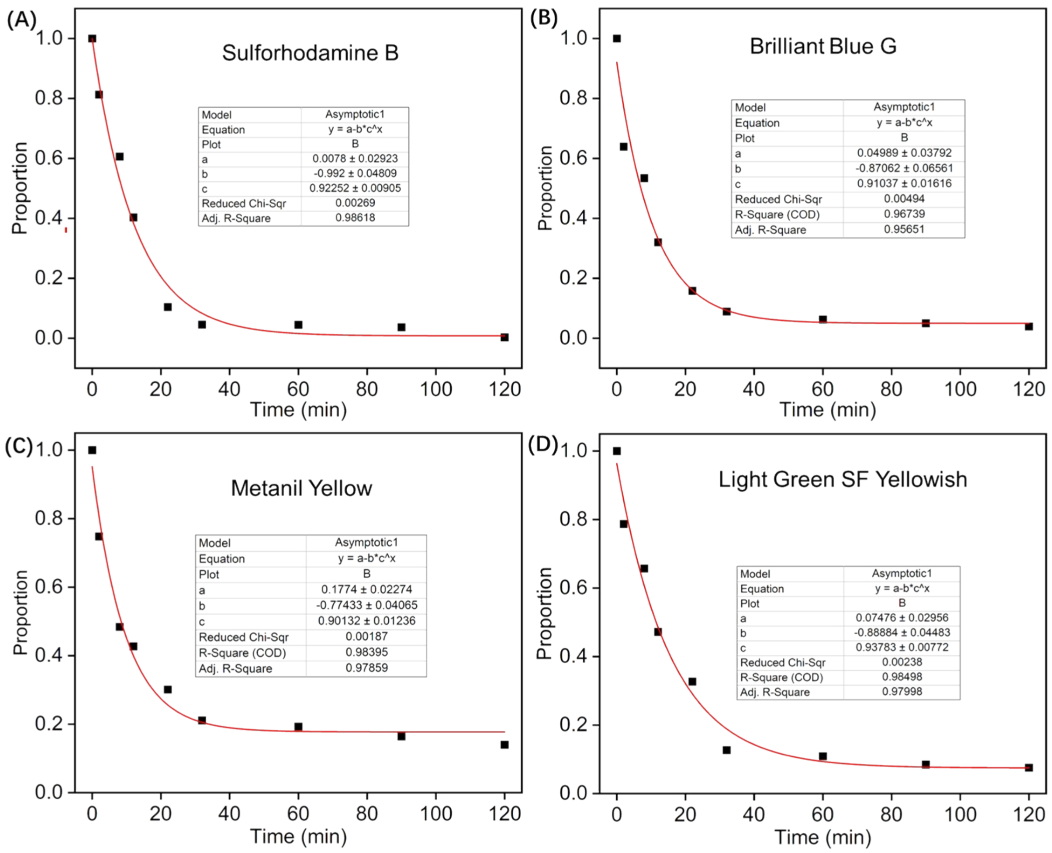
Volume : 8 ml

Amount of Melamine added : 5.225 mg

Saturation adsorption :

5.225 - 0.00466 x 8 x 126.15 = 0.5221 mg

Figure S48. (A) Standard curve of Melamine concentration and UV absorbance. (B) UV spectrum of excess Melamine solution adsorbed by 10 mg of **S** produced **S-G** and calculation of saturated adsorption capacity.



Model	Asymptotic1
Equation	y = a-b*c^x
Plot	B
a	0.0078 ± 0.02923
b	-0.992 ± 0.04809
c	0.92252 ± 0.00905
Reduced Chi-Sqr	0.00269
Adj. R-Square	0.98618

Model	Asymptotic1
Equation	y = a-b*c^x
Plot	B
a	0.04989 ± 0.03792
b	-0.87062 ± 0.06561
c	0.91037 ± 0.01616
Reduced Chi-Sqr	0.00494
R-Square (COD)	0.96739
Adj. R-Square	0.95651

Model	Asymptotic1
Equation	y = a-b*c^x
Plot	B
a	0.1774 ± 0.02274
b	-0.77433 ± 0.04065
c	0.90132 ± 0.01236
Reduced Chi-Sqr	0.00187
R-Square (COD)	0.98395
Adj. R-Square	0.97859

Model	Asymptotic1
Equation	y = a-b*c^x
Plot	B
a	0.07476 ± 0.02956
b	-0.88884 ± 0.04483
c	0.93783 ± 0.00772
Reduced Chi-Sqr	0.00238
R-Square (COD)	0.98498
Adj. R-Square	0.97998

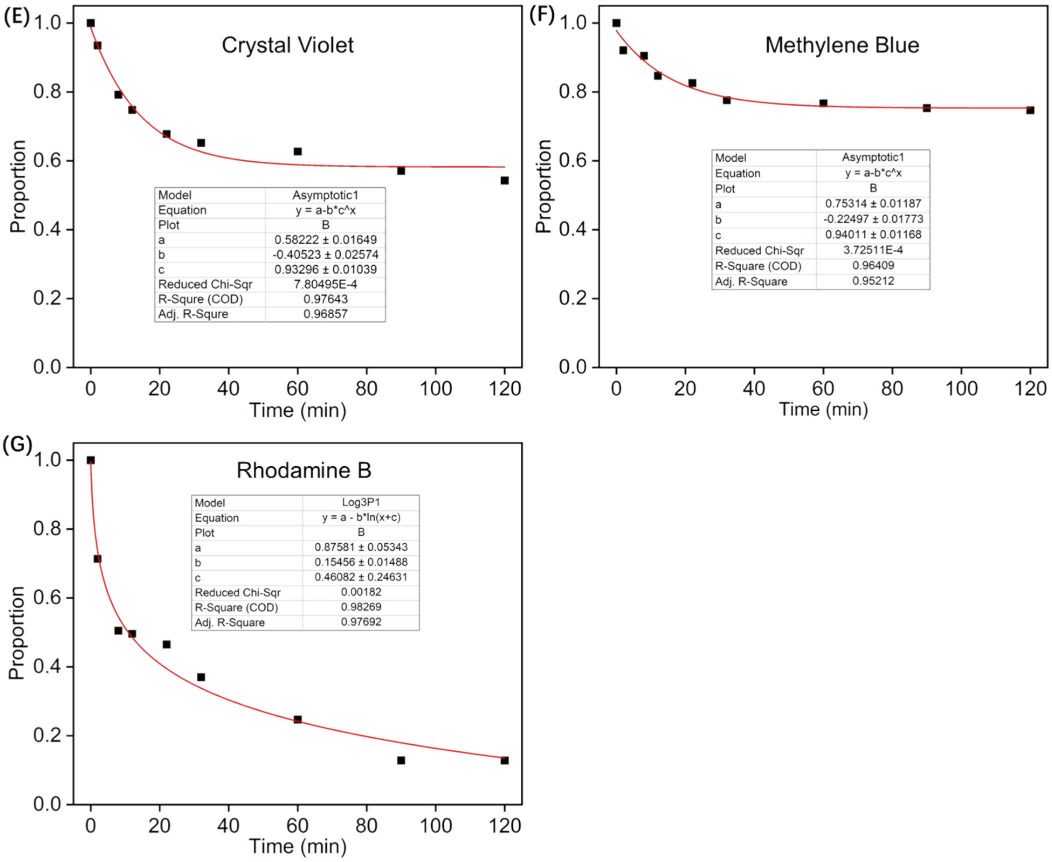


Figure S49. In the adsorption experiment of **S-G** on dye molecules, trend line fitted with model Exponential-Asymptotic-1 and Logarithm-Log3P1 of the proportion of dye residues in the solution with time. (A) Sulforhodamine B; (B) Brilliant Blue G; (C) Metanil Yellow; (D) Light Green SF Yellowish; (E) Crystal Violet; (F) Methylene Blue; (G) Rhodamine B.

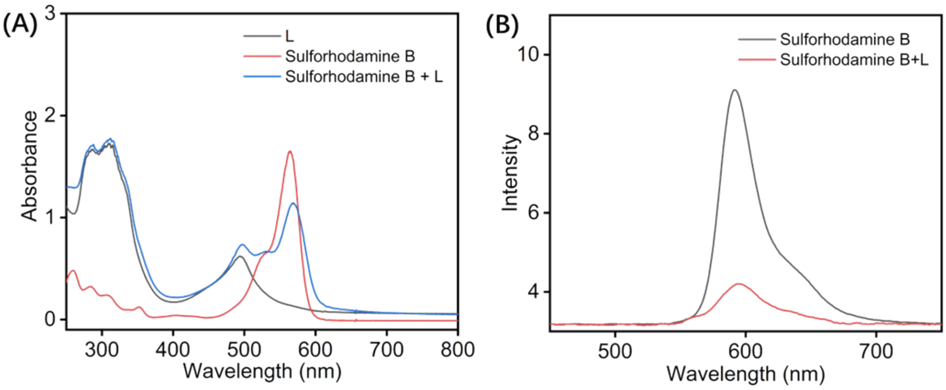


Figure S50. (A) UV spectra of L (c = 9.70 × 10^{-6} M), Sulforhodamine B (c = 2.50 × 10^{-5} M) and Sulforhodamine B with L mixed in CH_3CN/H_2O = 1:60 solvent at 298K; (B) Fluorescence spectra of Sulforhodamine B and Sulforhodamine B with L mixed solution (λ_{ex} = 563 nm).

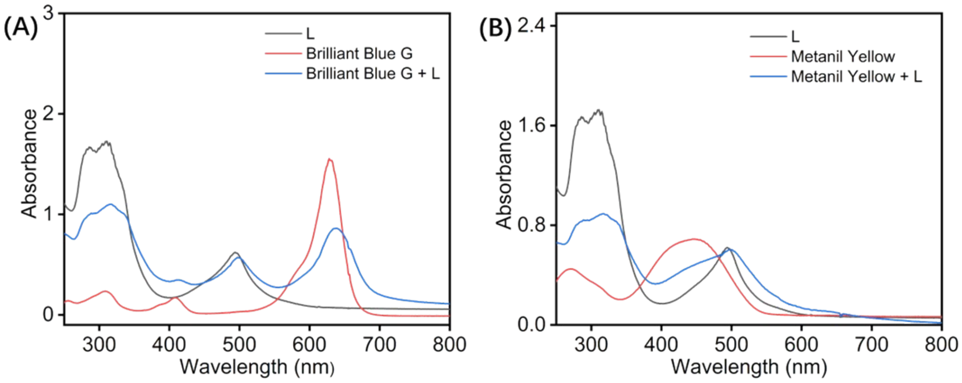


Figure S51. (A) UV spectra of L (c = 9.70 × 10^{-6} M), Brilliant Blue G (c = 2.27 × 10^{-5} M) and Brilliant Blue G with L mixed in CH_3CN/H_2O = 1:60 solvent at 298K; (B) UV spectra of L (c = 9.70 × 10^{-6} M), Metanil Yellow (c = 7.94 × 10^{-5} M) and Metanil Yellow with L mixed in CH_3CN/H_2O = 1:60 solvent at 298K.

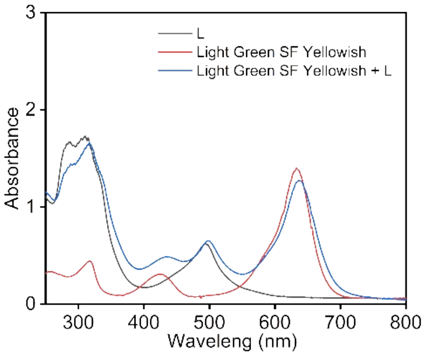


Figure S52. UV spectra of L (c = 9.70 × 10^{-6} M), Light Green SF Yellowish (c = 3.22 × 10^{-5} M) and Light Green SF Yellowish with L mixed in CH_3CN/H_2O = 1:60 solvent at 298K.

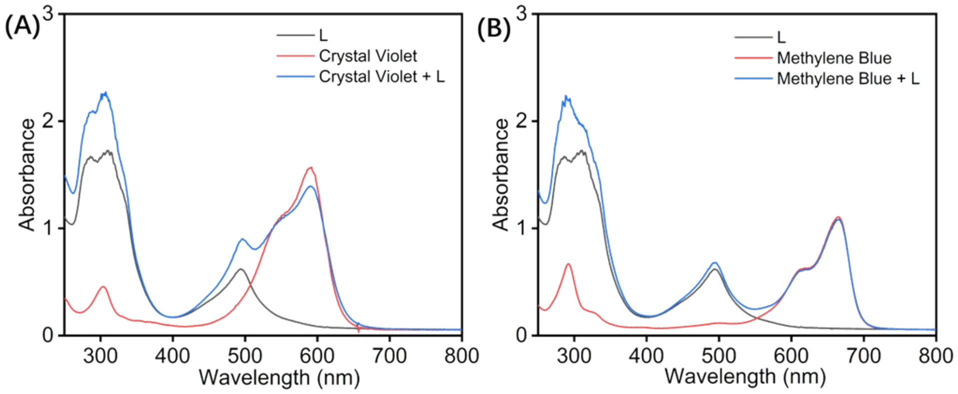


Figure S53. (A) UV spectra of L (c = 9.70 × 10^{-6} M), Crystal Violet (c = 1.90 × 10^{-5} M) and Crystal Violet with L mixed in CH_3CN/H_2O = 1:60 solvent at 298K; (B) UV spectra of L (c = 9.70 × 10^{-6} M), Methylene Blue (c = 6.95 × 10^{-5} M) and Methylene Blue with L mixed in CH_3CN/H_2O = 1:60 solvent at 298K.

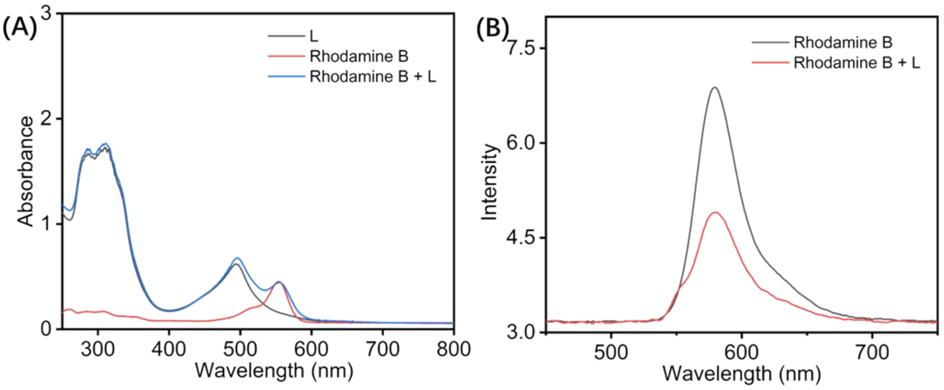


Figure S54. (A) UV spectra of L (c = 9.70 × 10^{-6} M), Rhodamine B (c = 2.91 × 10^{-5} M) and Rhodamine B with L mixed in CH_3CN/H_2O = 1:60 solvent at 298K; (B) Fluorescence spectra of Rhodamine B and Rhodamine B with L mixed solution (λ_{ex} = 554 nm).

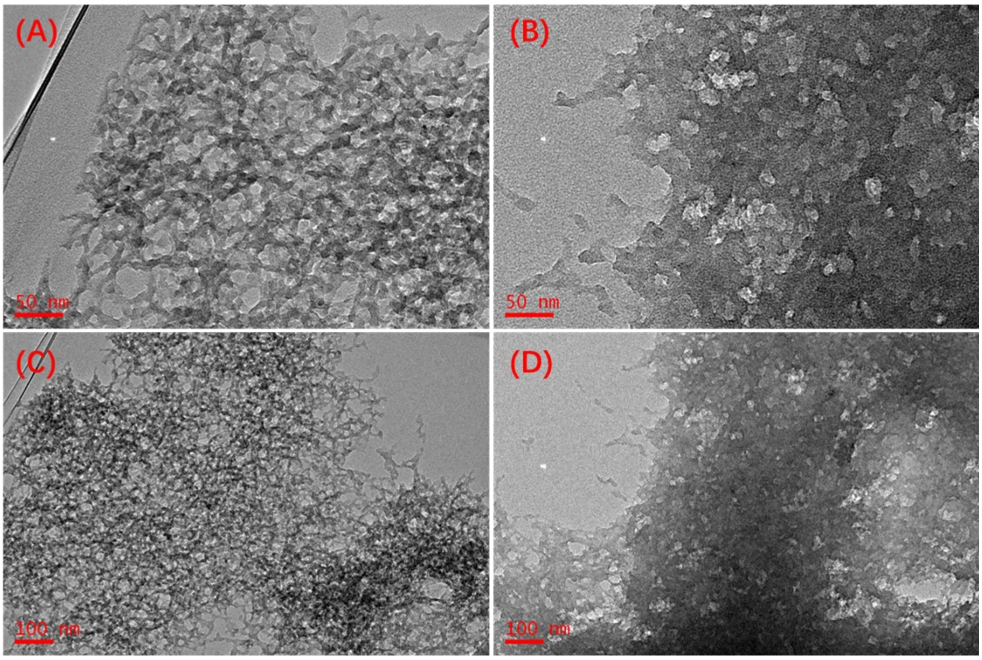


Figure S55. (A,C) TEM images of **S-G** in $CH_3CN:H_2O$（V:V=4：1）; (B,D) TEM images of **S-G** has adsorbed sulforhodamine B in H_2O.

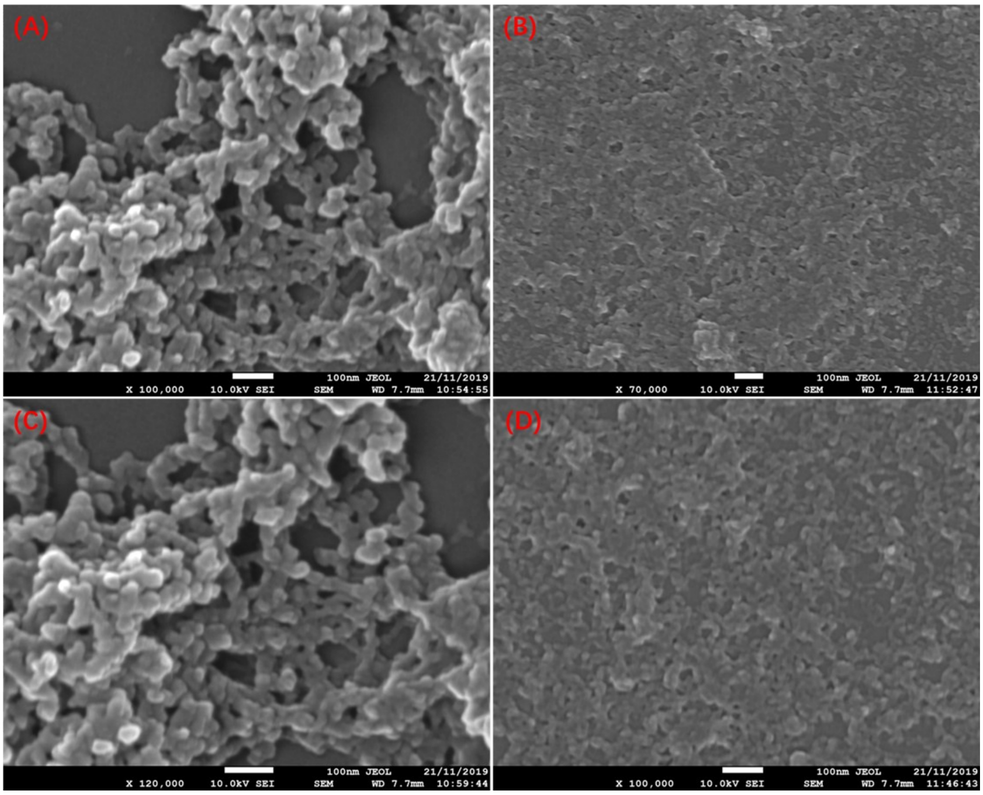
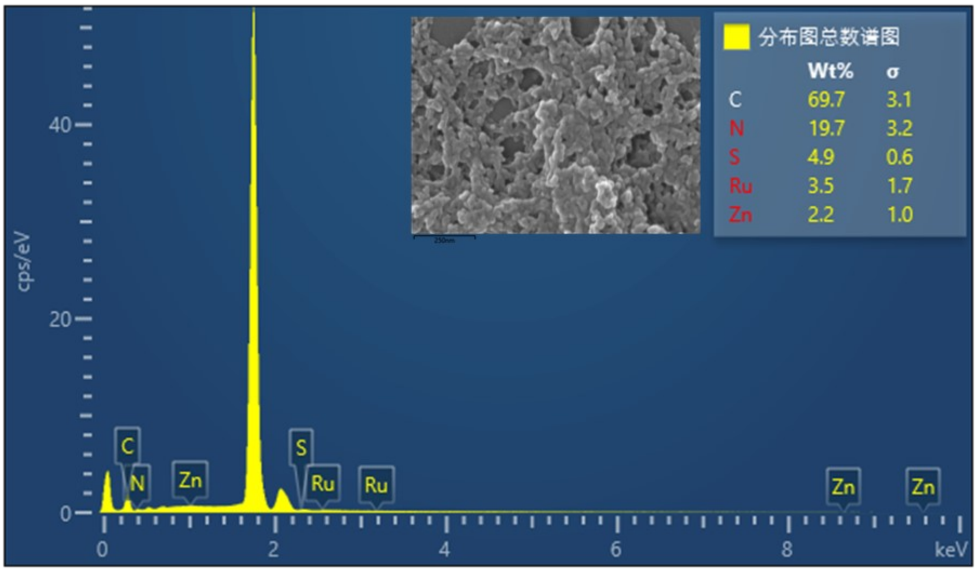


Figure S56. (A,C) SEM images of **S-G** in CH_3CN:H_2O（V:V=4：1）; (B,D) SEM images of **S-G** has adsorbed Sulforhodamine B in H_2O.



🟨 分布图总数谱图

	Wt%	σ
C	69.7	3.1
N	19.7	3.2
S	4.9	0.6
Ru	3.5	1.7
Zn	2.2	1.0

Figure S57. EDS of **S-G**.

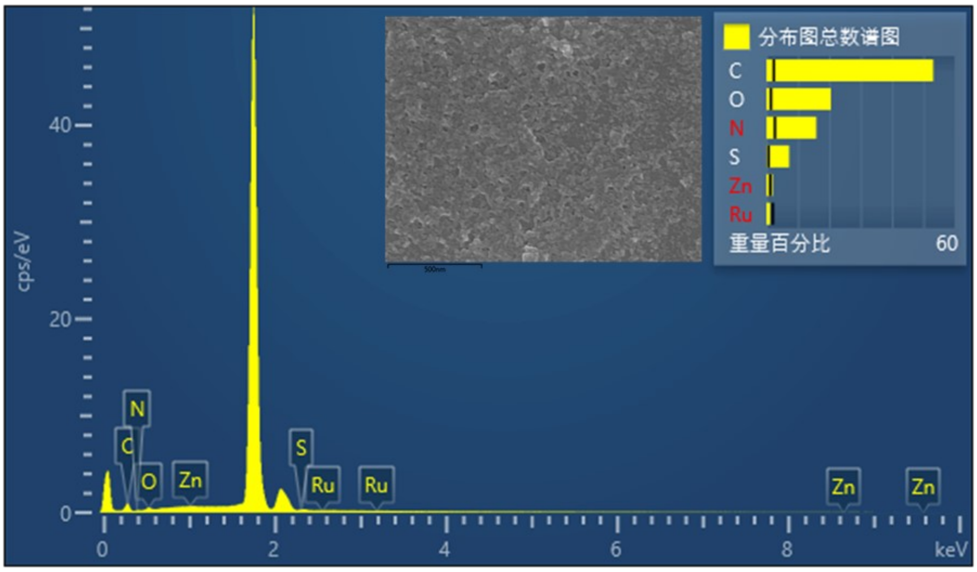


Figure S58. EDS of corresponding **S-G** after adsorbed Sulforhodamine B.

7. Reference.

1. J. L. Wang, X. Li, X. Lu, I. F. Hsieh, Y. Cao, C. N. Moorefield and G. R. Newkome, *J. Am. Chem. Soc.*, 2011, ***133***, 11450-11453.
2. D. Liu, H. Liu, B. Song, M. Chen, J. Huang, J. Wang and P. Wang, *Dalton Trans.*, 2018, ***47***, 14227-14232.
3. G. Wang, M. Chen, J. Wang, Z. Jiang, D. Liu, D. Lou, H. Zhao, K. Li, S. Li, T. Wu, Z. Jiang, X. Sun and P. Wang, *J. Am. Chem. Soc.*, 2020, ***142***, 7690-7698.