Supporting Information

An AIE active Y-shaped diimidazolylbenzene: aggregation and disaggregation for Cd^{2+} and Fe^{3+} sensing in aqueous solution

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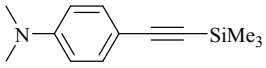
I. General remarks.

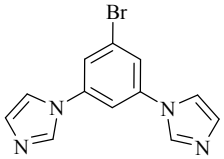
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. *N,N*-dimethylformamide (DMF) and triethylamine (Et_3N) were heated under reflux with calcium hydride, then distilled prior to use. Double-distilled water was used in the experiments.

NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). Absorption spectrum was obtained on a HITACHI U-2910 spectrophotometer. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer. The DLS measurements was conducted on a SEN 3690 instrument.

II. Synthesis of Y-dimb.

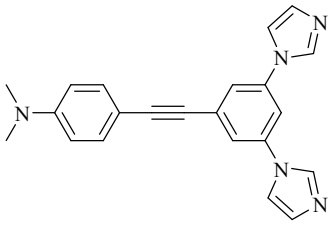


***N,N*-dimethyl-4-[(trimethylsilyl)ethynyl]aniline (1):** A mixture of 4-bromo-*N,N*-dimethylaniline (1.0 g, 5 mmol), $Pd(dppf)Cl_2$ (210.6 mg, 0.3 mmol), PPh_3 (131.2 mg, 0.5 mmol), CuI (95.2 mg, 0.5 mmol) and TMSA (2.14 mL 15.0 mmol) in Et_3N (10 mL) was reacted at 80 ºC overnight under N_2. The system was concentrated using rotavapor. The residue was passed through a silica gel column (PE/CH_2Cl_2 = 6/1, v/v) to give **1** as a yellow solid (1.01 g, 89% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 9H), 2.97 (s, 6H), 6.59 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H) ppm.



3,5-bis(1-imidazolyl)bromobenzene (2): A mixture of 1,3,5-tribromobenzene (5.25 g, 16.7 mmol), imidazole (2.25 g, 36.0 mmol), CuI (0.57 g, 3.3 mmol) and K_2CO_3 (8.29 g, 66.8 mmol) in DMF (50 mL) was reacted at 150 ºC for 10 h under N_2. The precipitates (inorganic salts) were filtered off, and the filtrate was concentrated in vacuo. The solid was then dispersed in ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated using rotavapor. The residue was passed through a silica gel column (CH_2Cl_2/MeOH = 30/1, v/v) to give **2** as a pale white solid (2.40 g, 55% yield). M.p. 180-182 ˚C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (s, 2H), 7.30 (s, 2H), 7.37 (t, J =

2.0 Hz, 1H), 7.56 (d, J = 2.0 Hz, 2H), 7.90 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.2, 118.1, 123.3, 124.8, 131.5, 135.6, 139.7 ppm.



4-{[3,5-di(1*H*-imidazol-1-yl)phenyl]ethynyl}-*N*,*N*-dimethylaniline (Y-dimb): A mixture of compound **1** (0.96 g, 3.6 mmol), compound **2** (0.87 g, 3.0 mmol), $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol), CuI (0.07 g, 0.36 mmol) and 50% KOH aqueous solution (1.6 mL) in Et_3N/THF (1:2, 13.5 mL) was reacted at 80 ºC overnight under N_2. The system was concentrated using rotavapor, and then the residue was passed through a silica gel column (CH_2Cl_2/CH_3OH = 30/1, v/v) to give **Y-dimb** as a yellow solid (0.72 g, 68% yield). M.p. 202-204 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.68 (d, J = 8.8 Hz, 2H), 7.26 (s, 2H), 7.31 (s, 1H), 7.35 (s, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.50 (s, 2H), 7.94 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.2, 85.4, 94.8, 108.3, 111.9, 118.2, 122.5, 128.2, 131.2, 133.2, 138.8, 150.8 ppm. HRMS (ESI^+): calcd for $C_{22}H_{20}N_5$ $[M+H]^+$ 354.1713, found 354.1707.

III. Absorption and fluorescence emission spectra of Y-dimb.

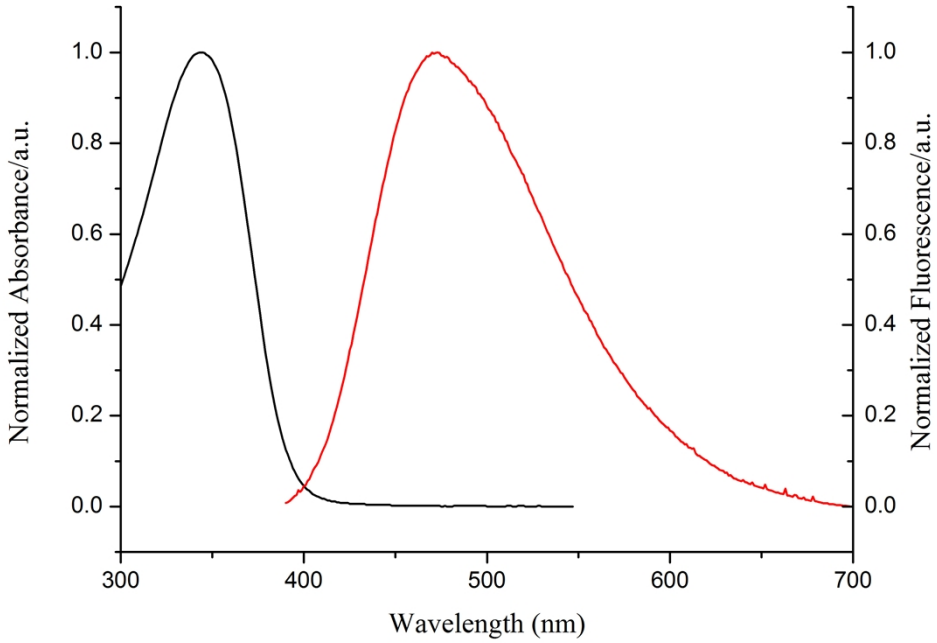


Fig. S1 Normalized absorption (black line) and fluorescence emission (red line) spectra of **Y-dimb** (20 μM) in MeCN.

IV. Fluorescence spectra of Y-dimb in the MeCN/water mixtures.

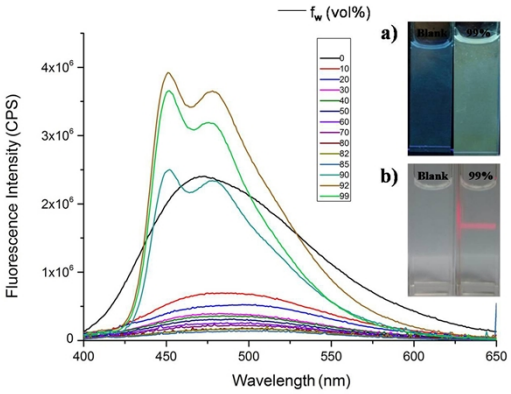


Fig. S2 The fluorescence spectra of **Y-dimb** (20 μM) in MeCN/water mixtures with different fractions of water. Excited at 359 nm. Inset: photos of a) **Y-dimb** in MeCN and CH_3CN/water (1:99, v/v) under UV light and b) the Tyndall phenomenon.

V. Fluorescence titration of Y-dimb with Cd^{2+}.

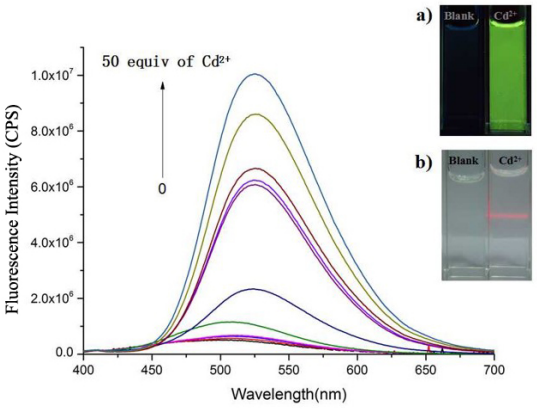


Fig. S3 The fluorescence spectra of **Y-dimb** (20 μM) in MeCN/water (2:8, v/v) upon addition of Cd^{2+} from 0 to 50 equiv. Inset: photos of a) **Y-dimb** in the presence of 50 equiv. of Cd^{2+} under UV light and b) the Tyndall phenomenon.

VI. Competitive experiment for Cd^{2+} sensing.

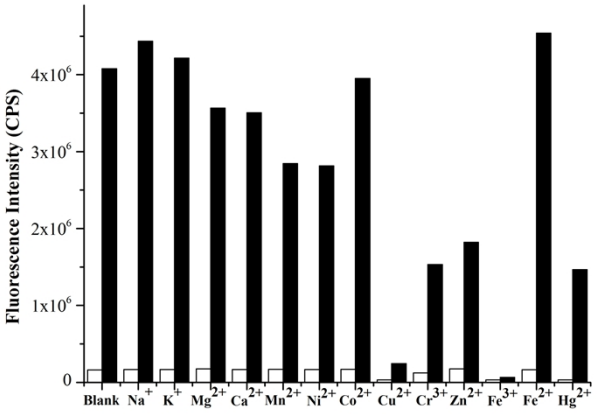


Fig. S4 The histogram of the fluorescence intensities of **Y-dimb** (20 μM) in MeCN/water (2:8, v/v) upon addition of 50 equiv. of blank, Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Fe^{3+}, Fe^{2+} and Hg^{2+} (white bar), and the subsequent addition of 50 equiv. of Cd^{2+} (black bar).

VII. Fluorescence quenching of Y-dimb by Fe^{3+}.

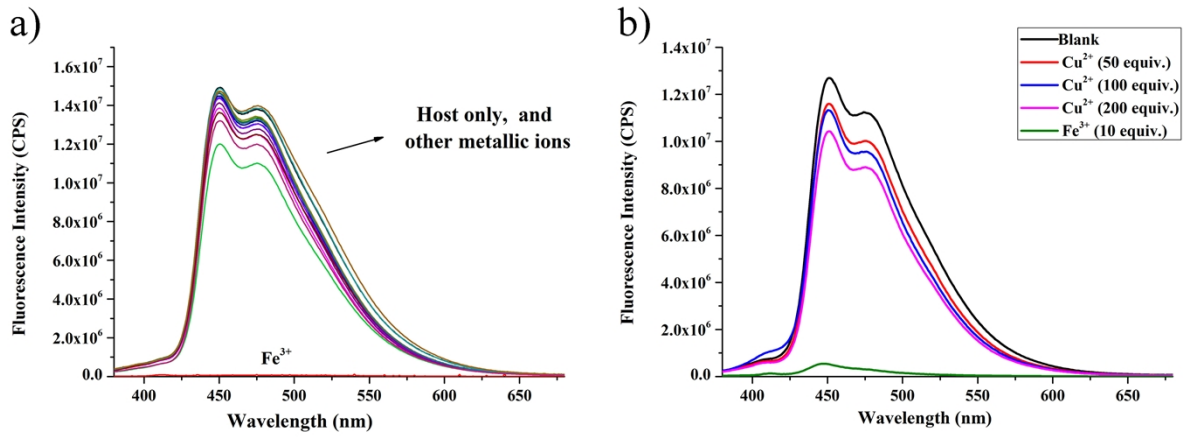


Fig. S5 The fluorescence spectra of **Y-dimb** (20 μM) in MeCN/water (1:99, v/v) upon addition of 10 equiv. of Fe^{3+} and a) 50 equiv. of Fe^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cr^{3+}, Ag^+, K^+ and Hg^{2+}; and b) 50, 100 and 200 equiv. of Cu^{2+}, respectively.

VIII. DLS measurements.

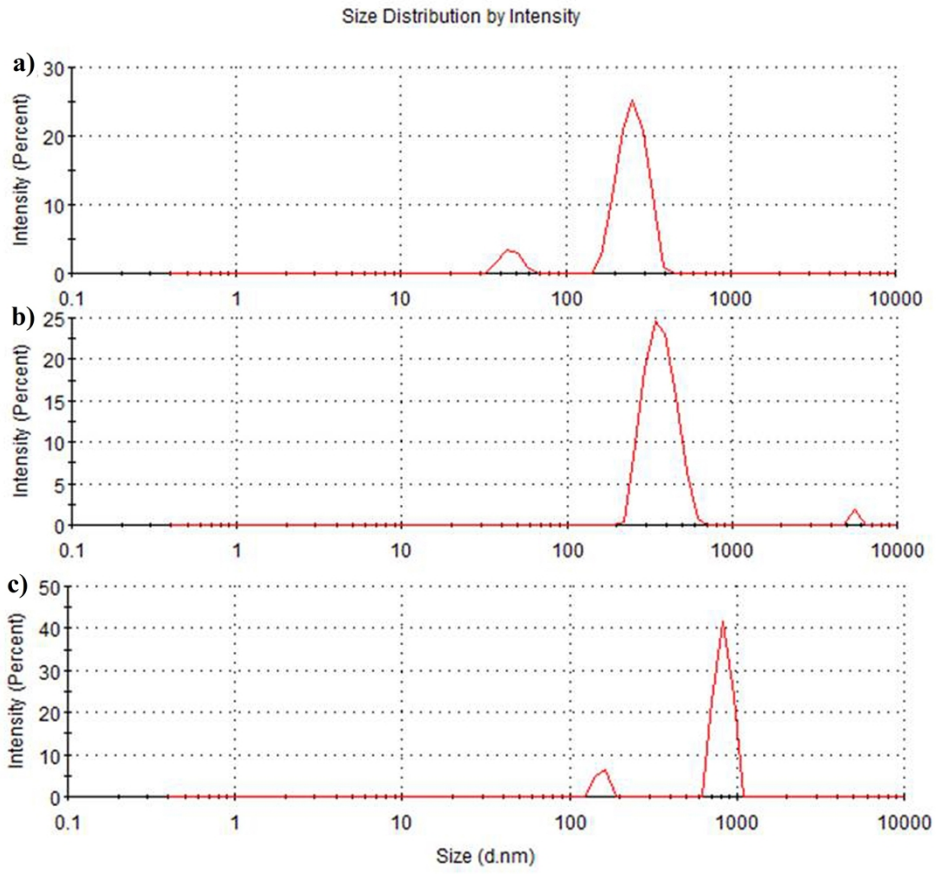


Fig. S6 DLS profiles of **Y-dimb** (20 μM) in MeCN/water mixtures with water fractions of a) 80%; b) 85%; and c) 92%, respectively.

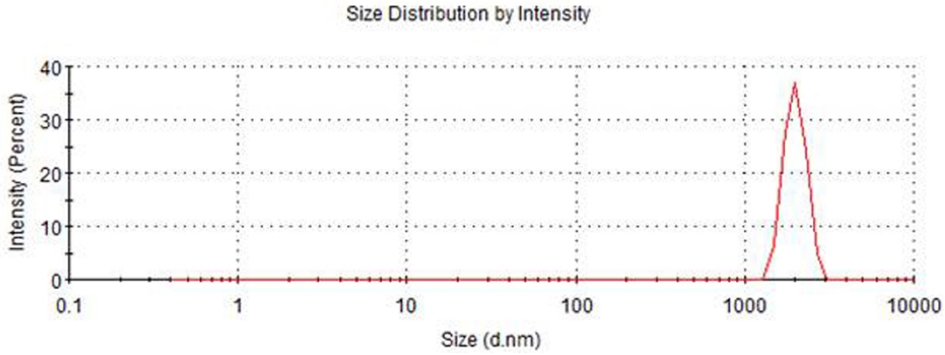


Fig. S7 DLS profile of **Y-dimb** (20 μM) in 2:8 (v:v) MeCN/water mixture with 50 equiv of Cd^{2+}.

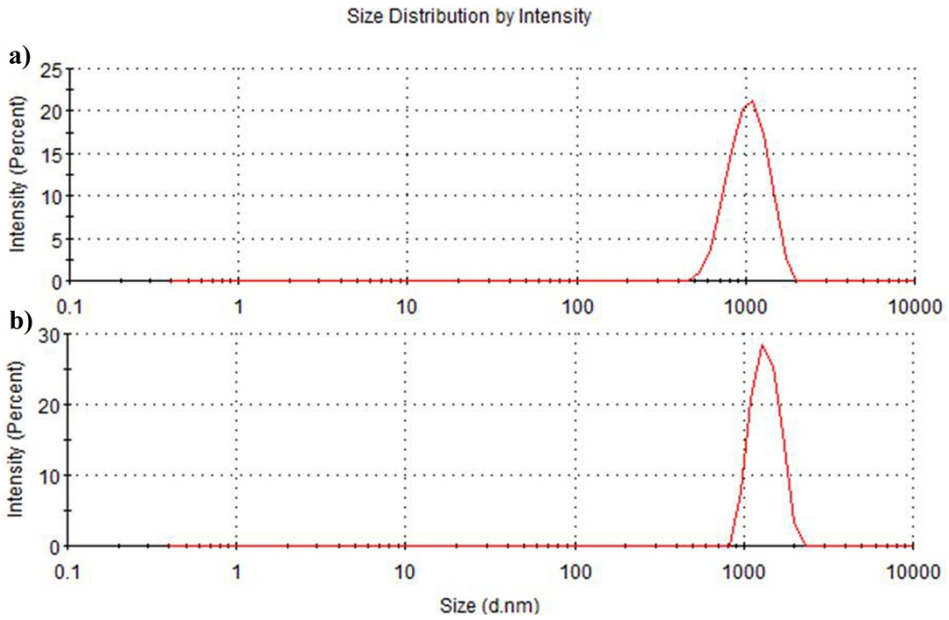
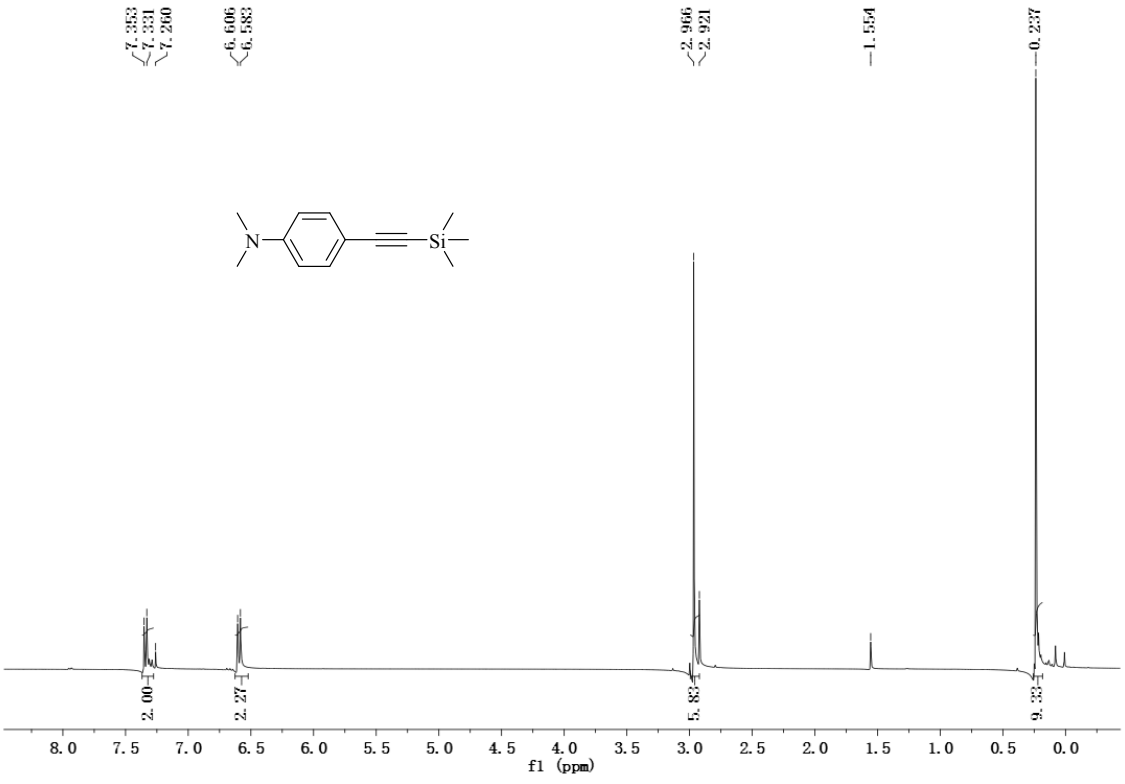
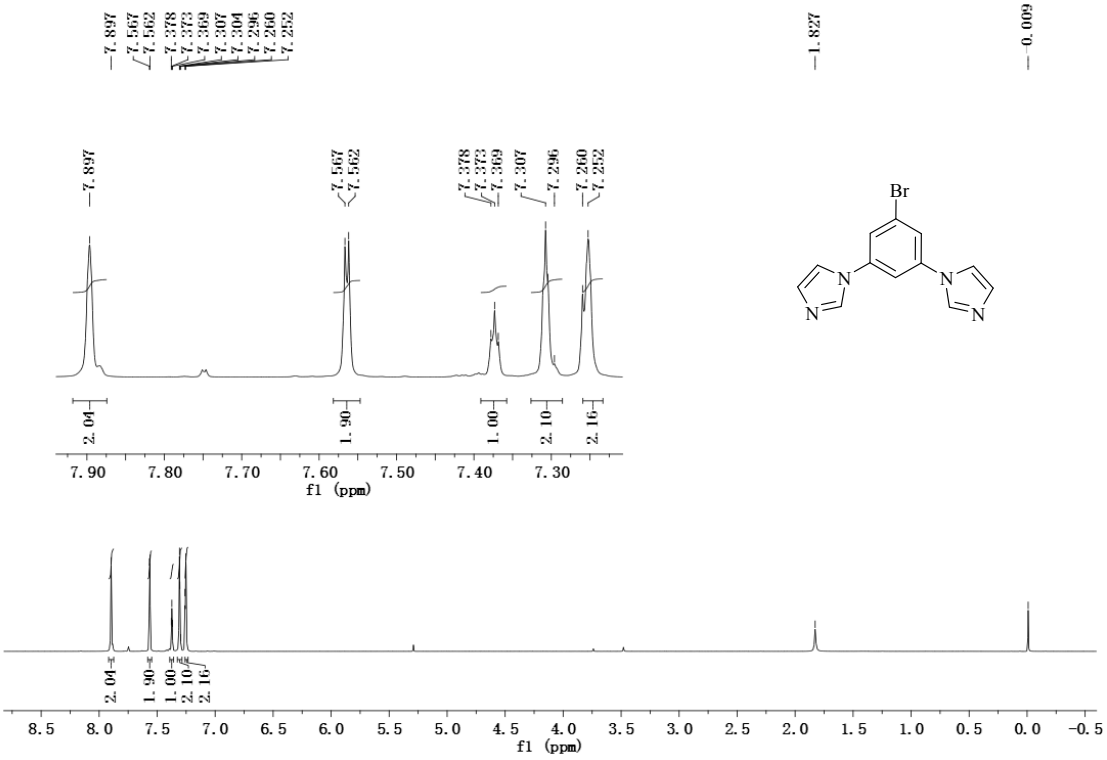
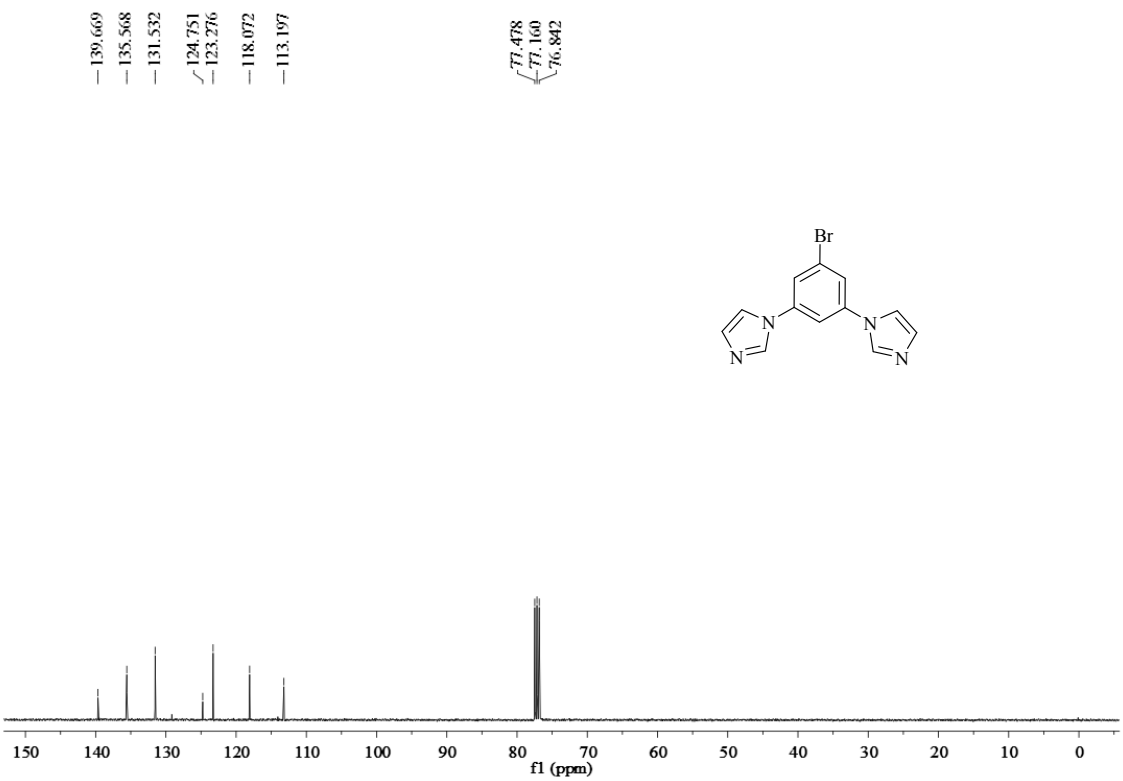


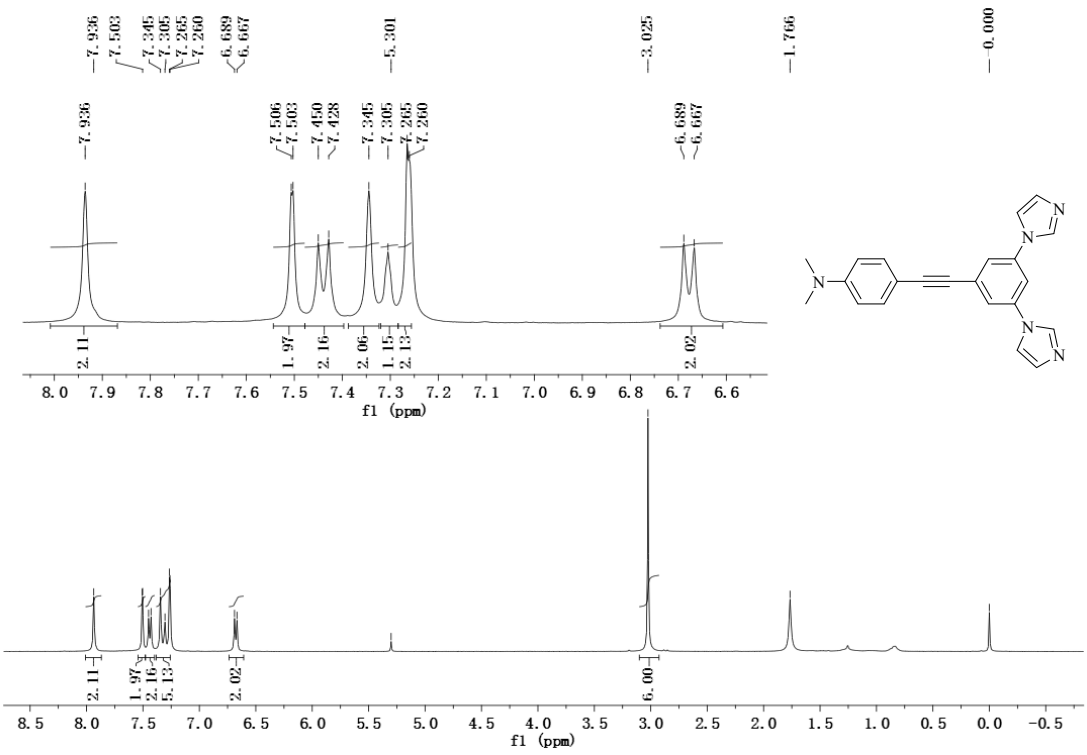
Fig. S8 DLS profiles of Fe^{3+} (1 mM) in 2:8 (v:v) MeCN/water mixture a) without and b) with **Y-dimb** (20 μM), respectively.

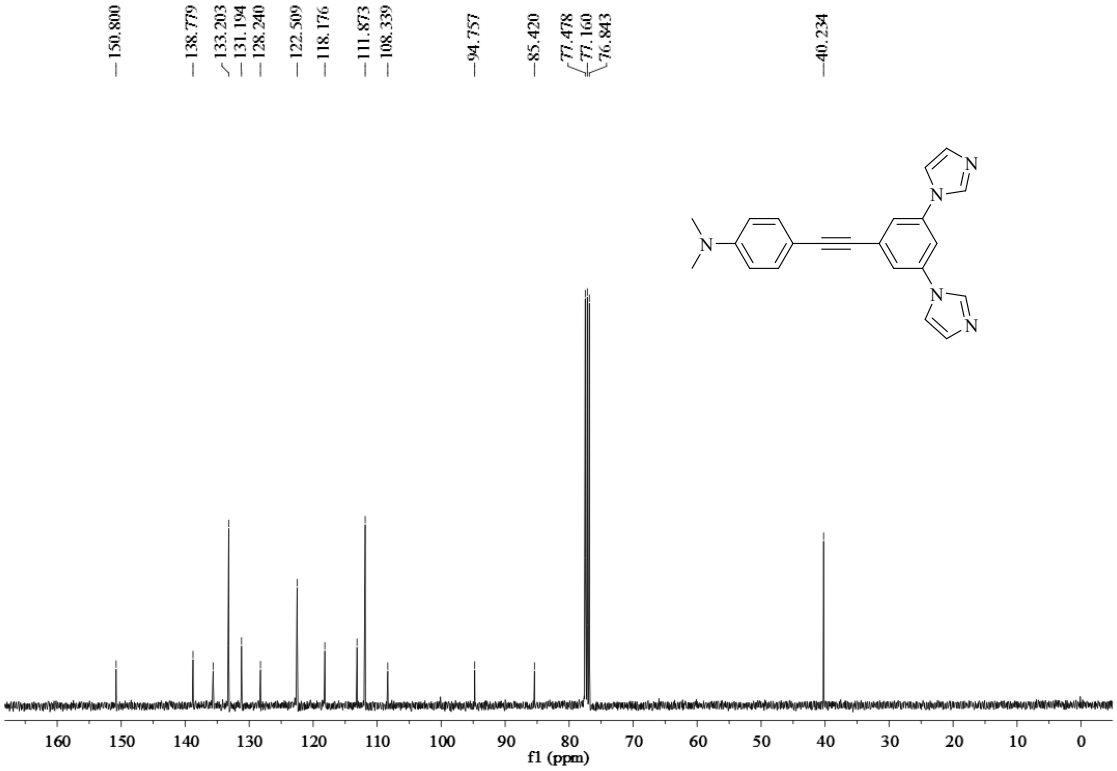
IX. Copies of ^{1}H NMR and ^{13}C NMR Spectra.




7.897
7.567
7.562
7.378
7.373
7.369
7.307
7.296
7.260
7.252
1.827
0.009
Br
N
N
N
N
2.04
1.90
1.00
2.10
2.16
f1 (ppm)


139.669
135.568
131.532
124.751
123.276
118.072
113.197
77.478
77.160
76.842
Br
N
N
N
N
f1 (ppm)


7.936
7.503
7.345
7.305
7.265
7.260
6.689
6.667
5.301
3.025
1.766
0.000
2.11
1.97
2.16
2.06
1.15
2.13
2.02
6.00
f1 (ppm)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131.194
128.240
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94.757
85.420
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40.234
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)