

Supplementary Material for:

A Conformationally Switchable Fluorescent Oligophenol Foldamer for Selective Sensing of Copper(II) Ions

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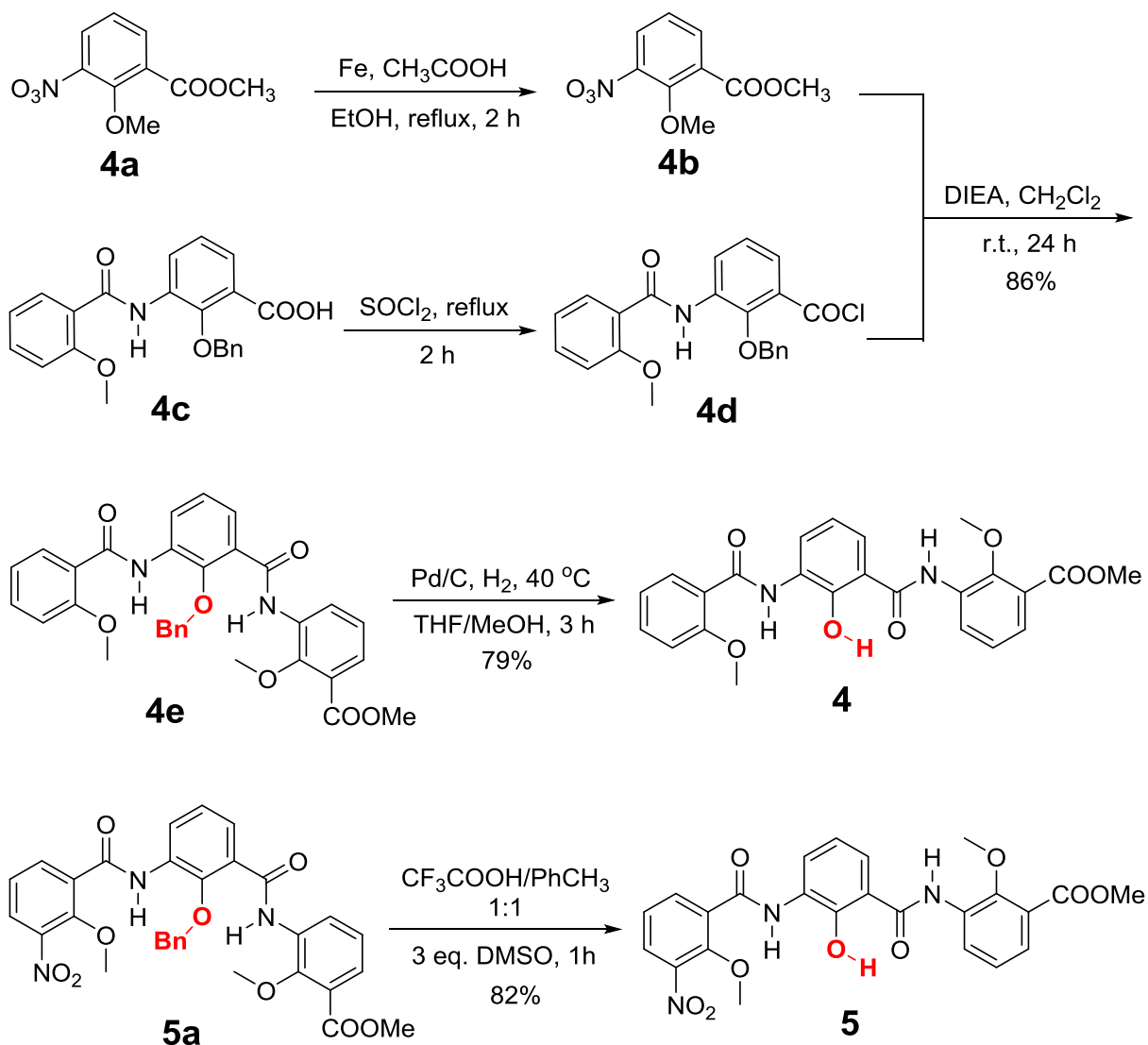
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1. General Remarks

All the reagents were obtained from commercial suppliers and used as received unless otherwise noted. Aqueous solutions were prepared from distilled water. The organic solutions from all liquid extractions were dried over anhydrous Na_2SO_4 for a minimum of 15 minutes before filtration. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates (0.25 mm thickness, 60F-254, E. Merck). Flash column chromatography was performed using pre-coated 0.2 mm silica plates from Selecto Scientific. Chemical yields refer to pure isolated substances. Mass spectra were obtained using the Instrumentation includes Finnigan MAT95XL-T and Micromass VG7035. ^1H NMR spectra were recorded on Bruker ACF-300 (300 MHz) or AVF500 spectrometers (500 MHz). The solvent signal of CDCl_3 was referenced at $\delta = 7.26$. Coupling constants (J values) are reported in Hertz (Hz). ^1H NMR data are recorded in the order: chemical shift value, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons that gave rise to the signal and coupling constant, where applicable. ^{13}C spectra are proton-decoupled and recorded on Bruker ACF300 (300 MHz) and ACF500 spectrometers (500 MHz). The solvent, CDCl_3 , was referenced at $\delta = 77$ ppm and DMSO-d_6 was referenced at $\delta = 39.5$. CDCl_3 (99.8%-Deuterated) and DMSO-d_6 (99.8%-Deuterated) was purchased from Aldrich and used without further purification. UV-vis absorption and fluorescence spectra were recorded on a Shimadzu UV-1700 spectrometer and a RF-5301 fluorometer respectively.

2. Scheme S1. Synthetic Route That Affords Trimers 4 and 5.

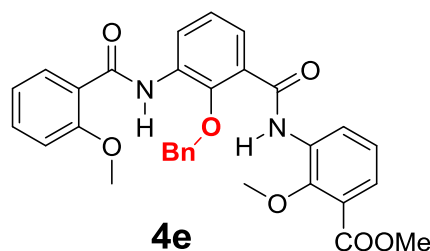


Synthesis of hexamer **2**, intermediates **4a**, **4c** and **5a** have been reported in the following journal publications:

- (1) B. Qin, C. L. Ren, R. J. Ye, C. Sun, K. Chiad, X. Y. Chen, Z. Li, F. Xue, H. B. Su, G. A. Chass and H. Q. Zeng, *J. Am. Chem. Soc.* 2010, **132**, 9564.
- (2) Sun, C. L. Ren, Y. C. Wei, B. Qin and H. Q. Zeng, *Chem. Commun.* 2013, **49**, 5307.

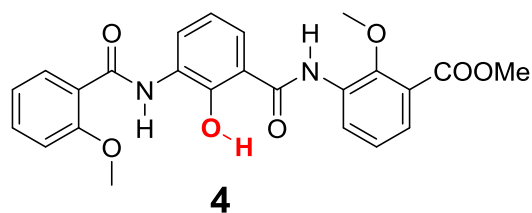
3. Synthetic Procedures and Characterizations

Compound 4e



To a solution of **4a** (0.24 g, 1.30 mmol) and iron (0.30 g, 5.20 mmol) in EtOH (20.0 mL) was added acetate acid (1.30 mL). The reaction was refluxed for 2 hours. After cooling, the solvent was evaporated and the residue was dissolved with CH₂Cl₂ and washed with water and Brine. The organic layer was dried over Na₂SO₄. Evaporation of the solvent gave the amine product **4b** used for the next step reaction without purification. A solution of **4c** (0.38 g, 1.00 mmol) in SOCl₂ (3.00 mL) was heated under reflux for 2 hours. Removal of the SOCl₂ generated acid **4d**, which was dissolved in dry CH₂Cl₂ (10.0 mL) to which the amine product **4b** and DIEA (0.34 mL, 2.00 mmol) in dry CH₂Cl₂ (10.0 mL) were added dropwise. The reaction was allowed to proceed for overnight. After washing with HCl solution, aqueous sat. NaHCO₃ and Brine, the organic layer was dried over Na₂SO₄. The residue was purified by column chromatography to give **4e** as a white solid. Yield: 0.46 g, 86%. ¹H NMR (500 MHz, CDCl₃) δ 10.45 (s, 1H), 9.89 (s, 1H), 8.76 (d, *J* = 8.1 Hz, 2H), 8.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.23 – 7.03 (m, 7H), 6.96 (d, *J* = 8.3 Hz, 1H), 5.01 (s, 2H), 3.96 (s, 3H), 3.84 (s, 3H), 3.69 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 165.9, 163.7, 163.4, 157.2, 149.2, 146.1, 134.7, 133.5, 133.1, 133.0, 132.6, 129.4, 128.9, 128.4, 127.9, 126.0, 125.5, 125.4, 125.2, 124.7, 124.2, 123.5, 121.5, 121.5, 111.3, 78.4, 62.2, 55.6, 52.2. MS-ESI: calculated for [M]⁺ (C₃₁H₂₈N₂O₇): m/z 540.6, found: m/z 540.5.

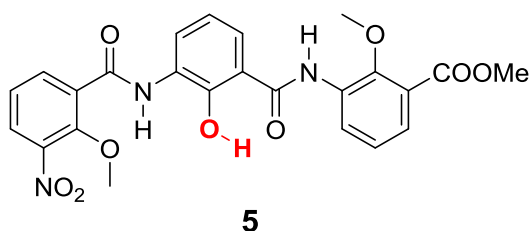
Compound 4



Compound **4e** (0.54 g, 1.00 mmol) was reduced by catalytic hydrogenation in THF/MeOH (v/v = 3/1, 16 mL) at 40 °C using Pd/C (0.11 g, 20%) as catalyst for 3 hours. The reaction mixture was then filtered and the residue was washed with CHCl₃ (2× 10.00ml) which

was removed under *vacuo* to give the solid. 5ml of MeOH was added to the solid and stirred for 1 hour then filtered to give product **4** as white solid. Yield: 0.36, 79%. ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.87 (s, 1H), 10.70 (s, 1H), 10.56 (s, 1H), 8.53 (d, *J* = 7.9 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.32 – 7.26 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 4.06 (s, 3H), 3.87 (s, 3H), 3.78 (s, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 168.6, 166.2, 163.4, 157.8, 153.4, 150.4, 134.2, 131.8, 130.6, 128.9, 128.5, 125.6, 124.7, 124.3, 123.2, 121.6, 121.5, 119.5, 116.1, 113.2, 62.4, 56.9, 52.8. HRMS-ESI: calculated for [M-Na]⁺ (C₂₄H₂₂N₂O₇Na): *m/z* 473.1319, found: *m/z* 473.1321.

Compound 5



To a solution of **5a** (0.29 g, 0.5 mmol) in toluene/trifluoroacetic acid (1:1, 5.0 mL) was added DMSO (0.12 g, 1.5 mmol). After 1 hr, the solvent was evaporated and the residue was dissolved with CH₂Cl₂ and washed with 1M HCl, and water (3 x 5 mL). The organic layer was dried over Na₂SO₄. The residue was recrystallized from methanol to give the pure product **5** as a white solid. Yield: 0.2 g, 82 %. ¹H NMR (300 MHz, CDCl₃) δ 12.82 (s, 1H), 10.42 (s, 1H), 8.95 (s, 1H), 8.75 (d, *J* = 8.0 Hz, 1H), 8.61 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.45 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.67 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 8.1 Hz, 1H), 7.04 (t, *J* = 8.1 Hz, 1H), 4.13 (s, 3H), 3.98 (s, 3H), 3.96 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 168.04, 165.55, 161.20, 151.64, 151.48, 149.54, 144.32, 136.38, 131.40, 128.99, 128.62, 128.40, 127.00, 124.74, 124.64, 124.27, 123.47, 119.88, 119.21, 113.97, 64.37, 62.64, 52.36. MS-ESI: calculated for [M]⁺ (C₂₄H₂₁N₃O₉): *m/z* 495.4, found: *m/z* 495.5.

5. X-Ray Crystallography Data Sheet for Trimers 4 and 5

Table S1. Crystal data and structure refinement for Trimer 4.

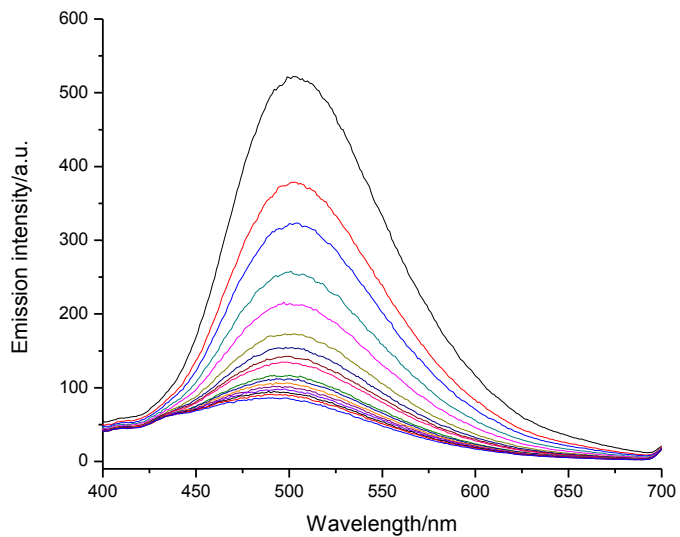
CCDC No:	1017708	
Empirical formula	C ₂₄ H ₂₂ N ₂ O ₇	
Formula weight	450.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.0883(19) Å	α = 90°.
	b = 9.8136(14) Å	β = 112.581(4)°.
	c = 16.084(2) Å	γ = 90°.
Volume	2053.3(5) Å ³	
Z	4	
Density (calculated)	1.457 Mg/m ³	
Absorption coefficient	0.108 mm ⁻¹	
F(000)	944	
Crystal size	0.60 x 0.24 x 0.20 mm ³	
Theta range for data collection	1.57 to 27.48°.	
Index ranges	-17<=h<=18, -12<=k<=12, -16<=l<=20	
Reflections collected	14175	
Independent reflections	4705 [R(int) = 0.0321]	
Completeness to theta = 27.48°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9786 and 0.9378	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4705 / 0 / 310	
Goodness-of-fit on F ²	1.093	
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1270	
R indices (all data)	R1 = 0.0596, wR2 = 0.1412	
Largest diff. peak and hole	0.450 and -0.289 e.Å ⁻³	

Table S2. Crystal data and structure refinement for Trimer **5•Na⁺**.

CCDC No:	1017709	
Empirical formula	C _{25.13} H _{25.88} N ₃ NaO ₁₁	
Formula weight	568.85	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 15.2734(12) Å	α = 90°.
	b = 15.273 Å	β = 90°.
	c = 23.031(2) Å	γ = 90°.
Volume	5372.6(6) Å ³	
Z	8	
Density (calculated)	1.407 Mg/m ³	
Absorption coefficient	0.125 mm ⁻¹	
F(000)	2373	
Crystal size	0.28 x 0.04 x 0.04 mm ³	
Theta range for data collection	1.60 to 25.00°.	
Index ranges	-18<=h<=17, -18<=k<=16, -25<=l<=27	
Reflections collected	31686	
Independent reflections	9464 [R(int) = 0.0722]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9950 and 0.9659	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9464 / 11 / 762	
Goodness-of-fit on F ²	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0818, wR2 = 0.1553	
R indices (all data)	R1 = 0.1212, wR2 = 0.1703	
Absolute structure parameter	0.1(7)	
Largest diff. peak and hole	0.220 and -0.202 e.Å ⁻³	

5. Fluorescence quenching of **3** by CuCl₂ in various concentrations

a)



b)

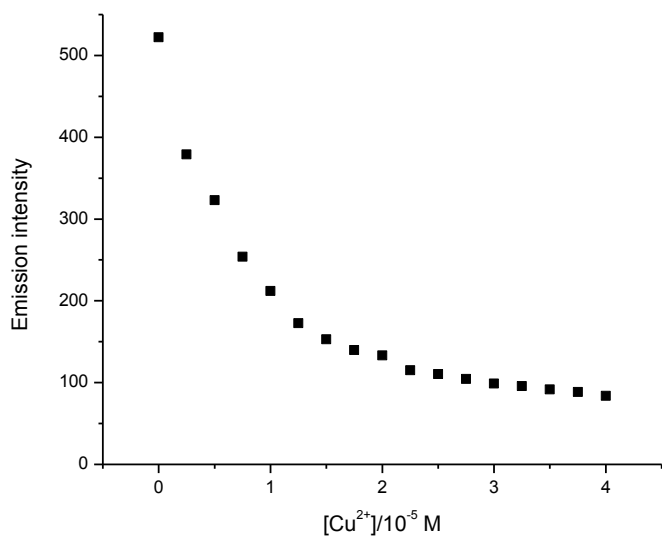


Figure S1. (a) Fluorescence spectra of oligophenol **3** (10 μM) in the presence of CuCl₂ at various concentrations from 2.5 - 40 μM in aqueous solution containing 1% of DMSO. (b) The corresponding fluorescence emission intensity at 505 nm with an excitation wavelength of 351 nm.

6. First Principle Molecular Modeling

All the calculations were carried out by utilizing the Gaussian 09¹ program package. The geometry optimizations were performed at the density functional theory (DFT) level, and the Becke's three parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP)² method was employed to do the calculations. The 6-31G(d,p)³ basis from the Gaussian basis set library has been used in all the calculations. The harmonic vibrational frequencies and zero-point energy corrections were calculated at the same level of theory. Single point energy were obtained at the B3LYP level in conjunction with the 6-311+G(2d, p) basis set with the use of the above optimized geometries, i.e., B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p).

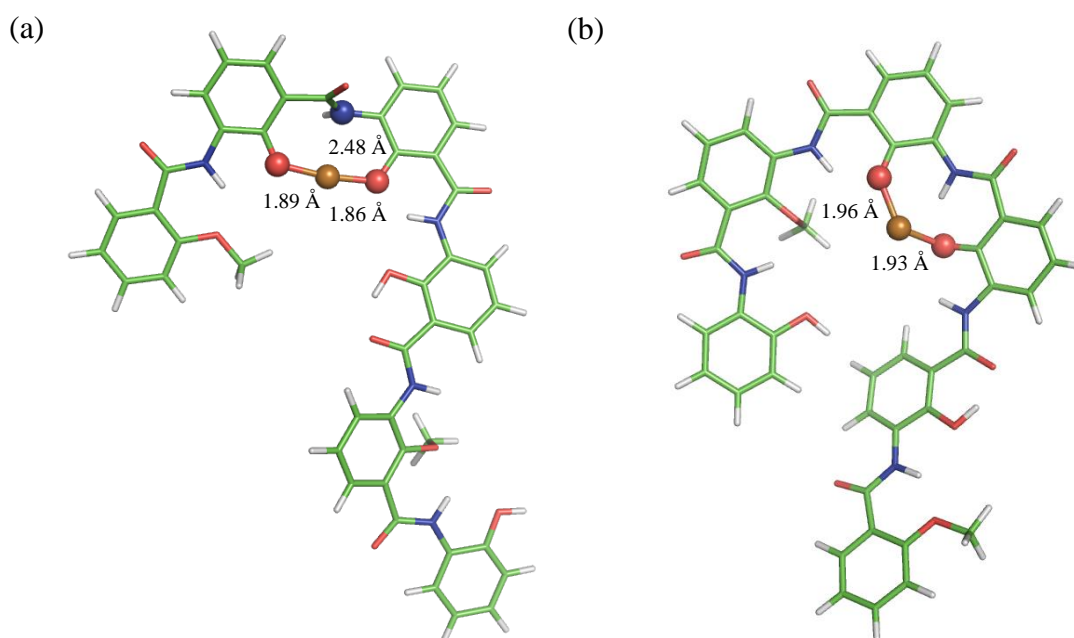


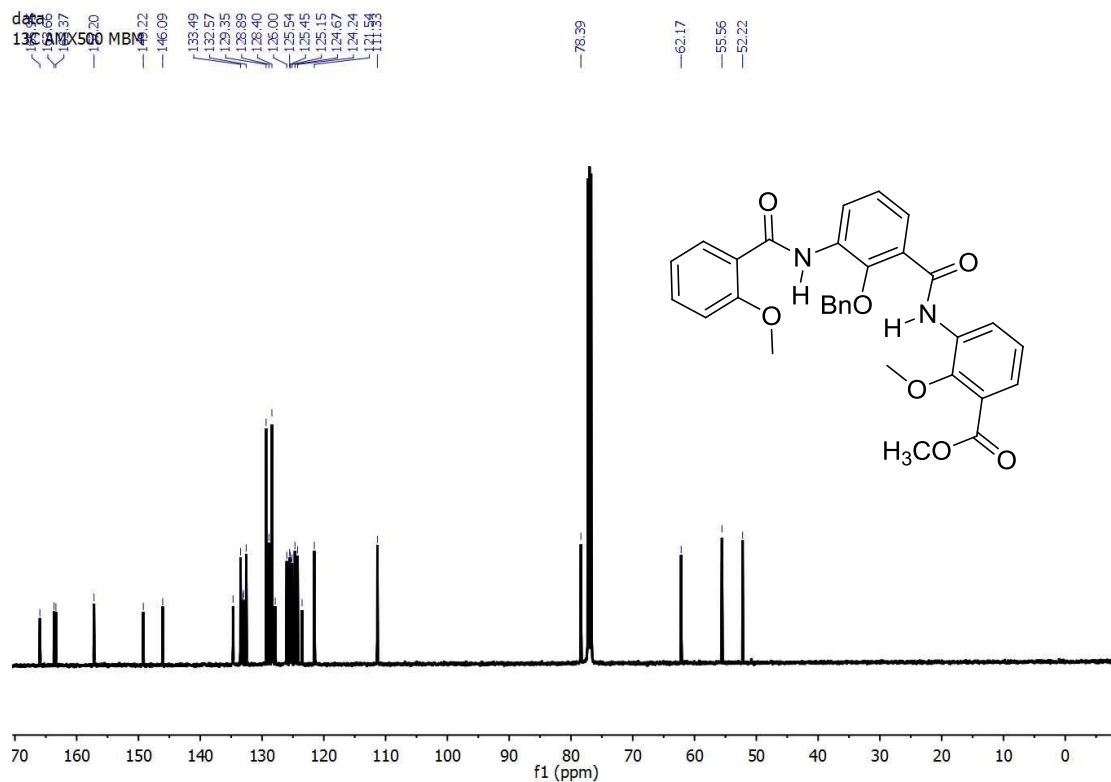
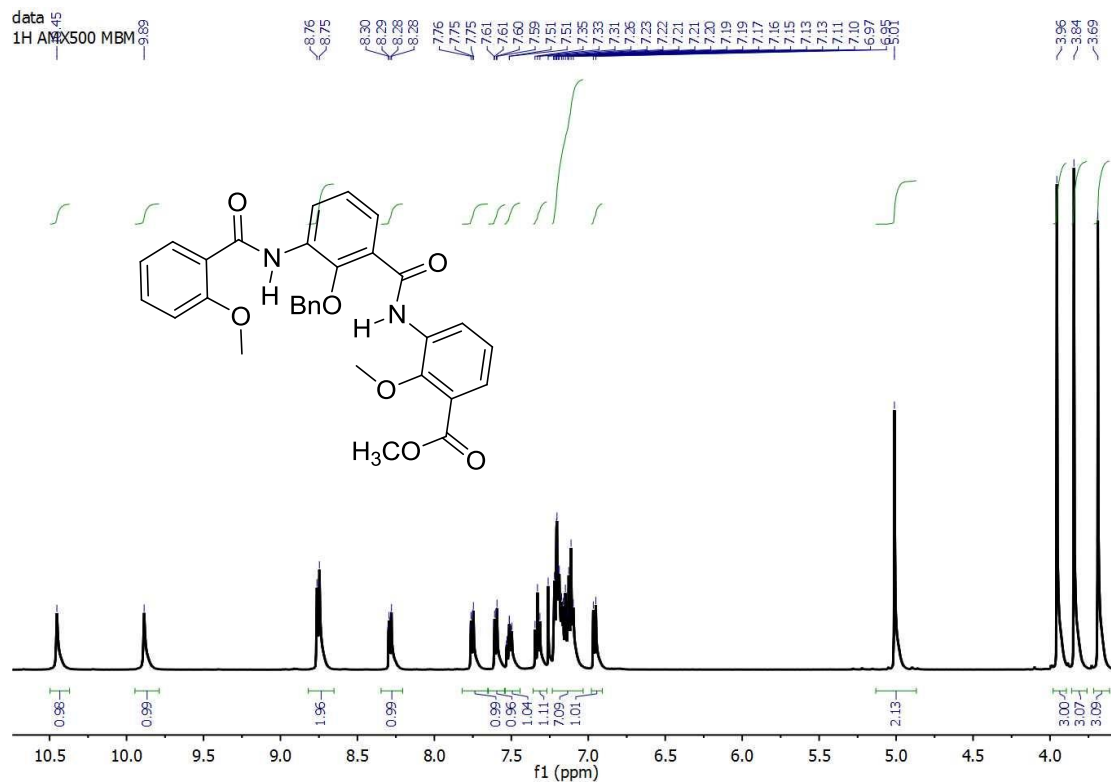
Figure S2. Computationally determined complexes between di-anionic oligomers **3_{ab}** or **3_{bc}** and Cu ions at the level of B3LYP/6-31G(d,p) using THF as the explicit solvent. Complex **3_{ab}•Cu²⁺** (a) turns out to be significantly more stable than **3_{bc}•Cu²⁺** (b) by 6.71 kcal/mol, suggesting **3_{ab}•Cu²⁺** as the predominant quenching species responsible for the observed quenching of **3** by Cu²⁺ ions. The distance between Cu ion and the N-atom is 2.48 Å.

¹ Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford CT, 2009.

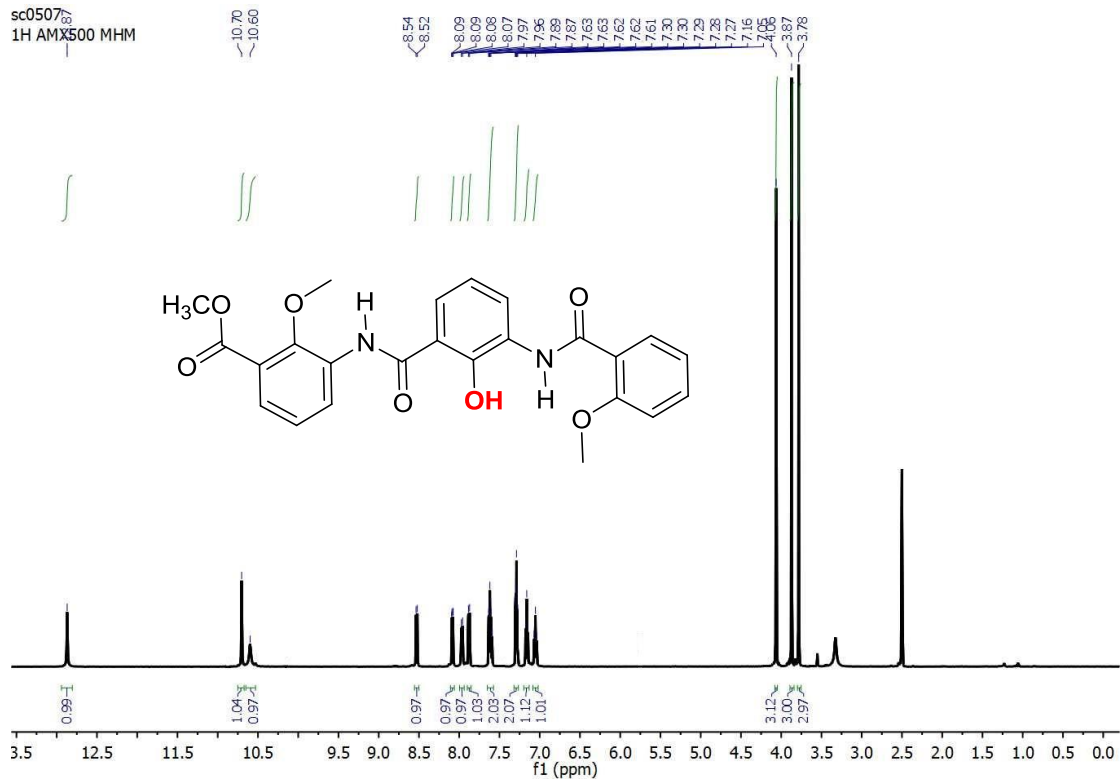
² Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.

³ Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, 94, 6081; Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, 89, 2193.

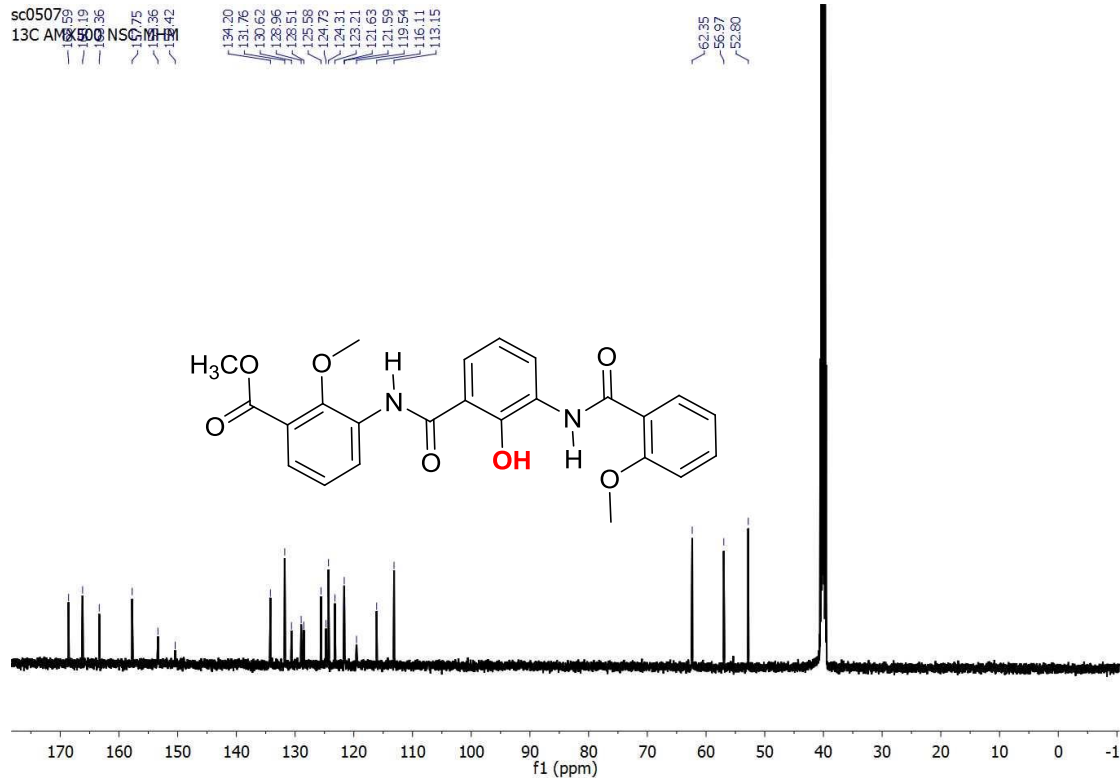
7. ^1H and ^{13}C NMR spectra

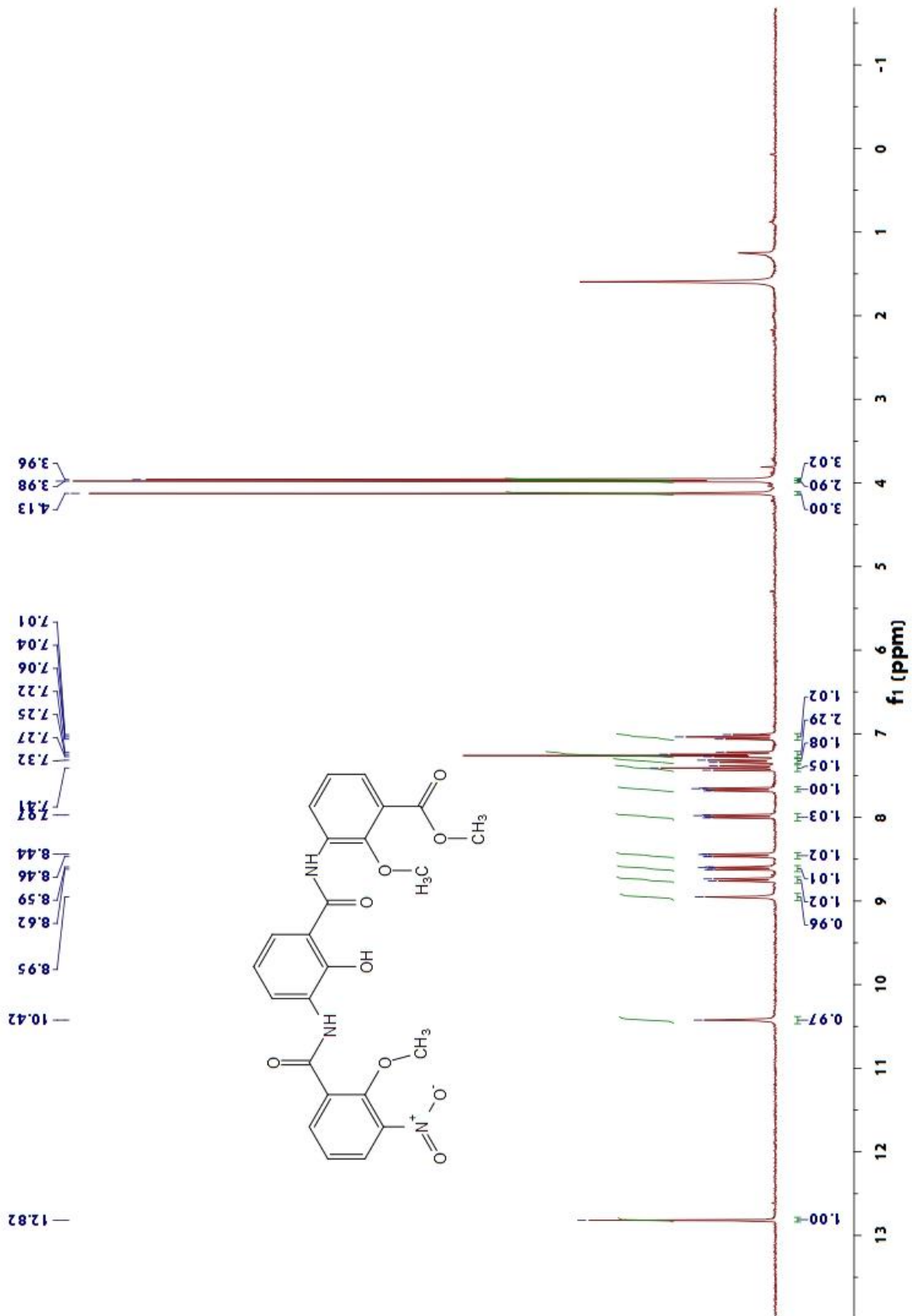


sc0507
1H AMX500 MHM



sc0507
13C AMX500 NSC-MH-M





168.04 —
 165.55 —
 161.20 —
 151.64 —
 151.48 —
 149.54 —
 144.32 —
 136.38 —
 128.62 —
 127.00 —
 124.64 —
 123.47 —
 119.88 —
 119.21 —
 113.97 —

