Supporting Information

Exploration of Energy Modulations in Novel RhB-TPE-Based Bichromophoric Materials via Interactions of Cu^{2+} ion under Various Semiaqueous and Micellar Conditions

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SYNTHESIS SECTION:

Synthesis of 4-(1,2,2-triphenylvinyl) phenol (1): Synthesis of **1** was performed by following the reported methods in the literature.[32]

Synthesis of 1,2-bis (4-hydroxyphenyl)-1,2-diphenylethene (2): Synthesis of **2** was performed by following the reported methods in the literature.[33]

General synthetic procedure for intermediates 3 and 5: The prepared compound 4-(1,2,2-triphenylvinyl)phenol **(1),** 1,2-bis(4-hydroxyphenyl)-1,2-diphenylethene **(2)** were charged into a cleaned dry 100 mL three necked round bottom flask followed by the addition of Acetone (20 mL) at room temperature under nitrogen gas atmosphere. K_2CO_3 was then added into the reaction mixture in one portion at room temperature and allowed to stir for 10-15 min. After that, 1,3-dibromoprpane was added dropwise into above reaction mixture at room temperature. Furthermore, resulting solution was refluxed at 60°C for overnight. Progress of reaction was monitored by TLC. After completion, reaction mixture was cooled to room temperature and directly evaporated to dryness under vacuum to get crude compound. Crude residue was then purified by using column chromatography over silica gel (2% ethyl acetate/ hexane) as eluent. Colorless liquids affording pure compounds were obtained.

Synthesis of (2-(4-(3-bromopropoxy) phenyl)ethene-1,1,2-triyl)tribenzene (3): 4-(1,2,2-triphenylvinyl)phenol (1) (1 g, 1 eq.), Acetone (20 mL), K_2CO_3 (0.99 g, 2.5 eq.), 1,3-dibromoprpane (1.17 mL, 4 eq.). A colorless liquid affording **(3)** (1.21 g) was obtained in a 90% yield.

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.08-7.14 (9H, m), 6.92-6.98 (6H, m), 6.85 (2H, d, *J* = 9.0 Hz), 6.69 (2H, d, *J* = 9.0 Hz), 3.97 (2H, t, *J* = 6.0 Hz, oxygen α-proton), 3.62 (2H, t, *J* = 6.0 Hz), 2.17 (2H, q, *J* = 6.0 Hz, Br α-proton).

^{13}C NMR (300 MHz, DMSO-d_6) δ (ppm): 157.7, 144.3, 141.0, 140.5, 136.4, 132.8, 131.5, 128.7, 127.2, 114.6, 65.9, 32.7, 32.1.

Synthesis of 1,2-bis(4-(3-bromopropoxy)phenyl)-1,2-diphenylethene (5): 1,2-bis(4-hydroxyphenyl)-1,2-diphenylethene (2) (1 g, 1 eq.), Acetone (20 mL), K_2CO_3 (1.89 g, 5 eq.), 1,3-dibromoprpane (2.23 mL, 8eq.). A colorless liquid affording (5) (1.49 g) was obtained in a 90% yield.

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.08-7.14 (6H, m), 6.92-6.99 (4H, m), 6.82-6.88 (4H, m), 6.67-6.74 (4H, m), 3.99 (4H, t, *J* = 6.0 Hz, oxygen α-proton), 3.63 (4H, t, *J* = 6.0 Hz), 2.20 (4H, q, *J* = 6.0 Hz, Br α-proton).

^{13}C NMR (300 MHz, DMSO-d_6) δ (ppm): 156.7, 143.6, 139.2, 135.8, 131.9, 130.7, 127.6, 126.2, 113.4, 66.9, 65.0, 31.8, 31.2, 25.0.

General synthetic procedure for intermediates 4 and 6:

Prepared compound (2-(4-(3-bromopropoxy)phenyl)ethene-1,1,2-triyl)tribenzene **(3),** 1,2-bis(4-(3-bromopropoxy)phenyl)-1,2-diphenylethene **(5)** were added into a cleaned dry 100 mL three necked round bottom flask at room temperature followed by the addition of dry DMF (40 mL) under nitrogen gas atmosphere. NaN_3 was added into the reaction mixture of intermediates **(3)** and **(5)** and allowed to reflux at 60°C for 10 h. Progresses of reactions were monitored by TLC.

After completion, reaction mixtures were cooled to room temperature. Reaction mixtures were then poured into a beaker containing diethyl ether (200 mL) and H_2O (200 mL). Organic layer was separated and washed with H_2O (200 mL x 2) and brine solution (200 mL x 2) and dried over $MgSO_4$, filtered and evaporated to dryness. Crude residues were subjected to column chromatography (silica gel, hexane/ethyl acetate: 9/1 to 6/4). Colorless liquids of desired intermediates **(4)** and **(6)** were recovered.

Synthesis of ((2-(4-(3-azidopropoxy)phenyl)ethene-1,1,2-triyl)tribenzene) (4): (2-(4-(3-bromopropoxy) phenyl) ethene-1,1,2-triyl) tribenzene **(3)** (1 g, 1 eq.), DMF (40 mL), NaN_3 (0.41 g, 3 eq.). A colorless liquid **(4)** was recovered (0.83 g) in a 91% yield.

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.08-7.14 (9H, m), 6.94-6.98 (6H, m), 6.84 (2H, d, *J* = 9.0 Hz), 6.68 (2H, d, *J* = 9.0 Hz), 3.92 (2H, t, *J* = 6.0 Hz, oxygen α-proton), 3.46 (2H, t, *J* = 6.0 Hz), 1.92 (2H, q, *J* = 6.0 Hz, Br α-proton).

^{13}C NMR (300 MHz, DMSO-d_6) δ (ppm): 157.9, 144.4, 141.2, 140.7, 136.5, 132.9, 131.7, 128.8, 127.4, 114.7, 68.0, 65.4, 48.7, 29.1, 26.1.

Synthesis of (1,2-bis(4-(3-azidopropoxy)phenyl)-1,2-diphenylethene) (6): 1,2-bis(4-(3-bromopropoxy)phenyl)-1,2-diphenylethene **(5)** (1 g, 1 eq.), DMF (40 mL), NaN_3 (0.32 g, 3 eq.). A colorless liquid **(6)** was recovered (0.79 g) in a 91% yield.

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.07-7.15 (6H, m), 6.98 (4H, m), 6.88-6.93 (4H, m), 6.67-6.70 (4H, m), 3.95 (4H, t, *J* = 6.0 Hz, oxygen α-proton), 3.48 (4H, t, *J* = 9.0 Hz), 1.93 (4H, q, *J* = 6.0 Hz, Br α-proton).

^{13}C NMR (300 MHz, DMSO-d_6) δ (ppm): 157.2, 144.2, 139.7, 136.2, 132.4, 131.2, 128.2, 126.7, 114.2, 64.8, 48.1, 28.5.

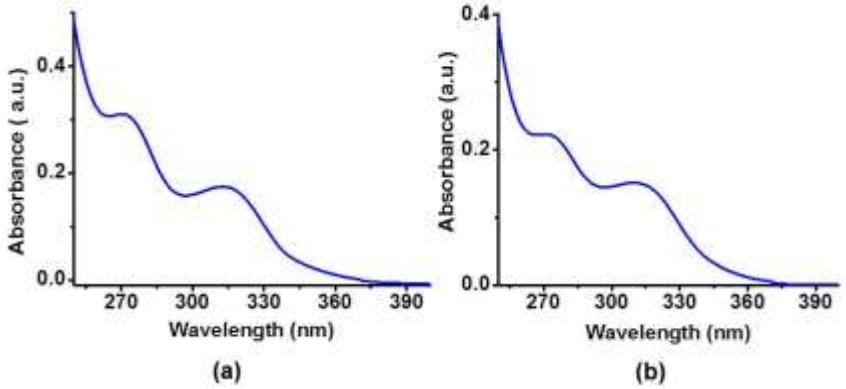


Figure S1. (a) UV-Vis spectra of **TR-A** (4 μM) (b) UV-Vis spectra of **TR-B** (4 μM) in CH_3CN solvent medium.

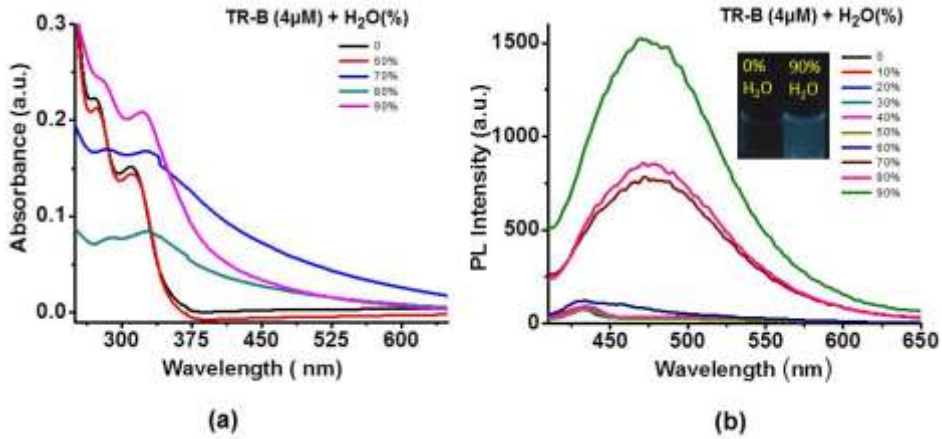


Figure S2. (a) UV-Vis spectra of **TR-B** with increasing water fractions: 0, 50, 60, 70, 80, and 90%. (b) PL spectra of **TR-B** with increasing water fractions: 0, 10, 20, 30, 40, 50, 60, 70, 80, and 90%, Inset: photoimages of **TR-B** under UV lamp in the absence and presence (90%) of water. with an excitation wavelength at λ_{ex} = 380 nm.

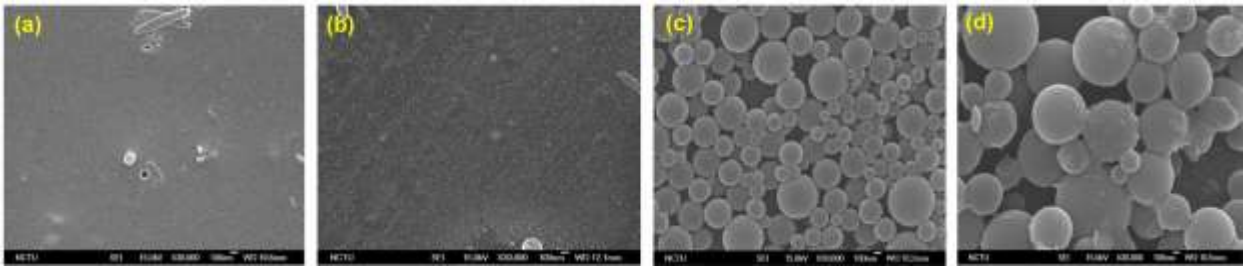


Figure S3. Morphological images of (a) **TR-B** in CH_3CN (b) **TR-B** at 60% water content (c) **TR-B** at 70% water content (d) **TR-B** at 90% water content.

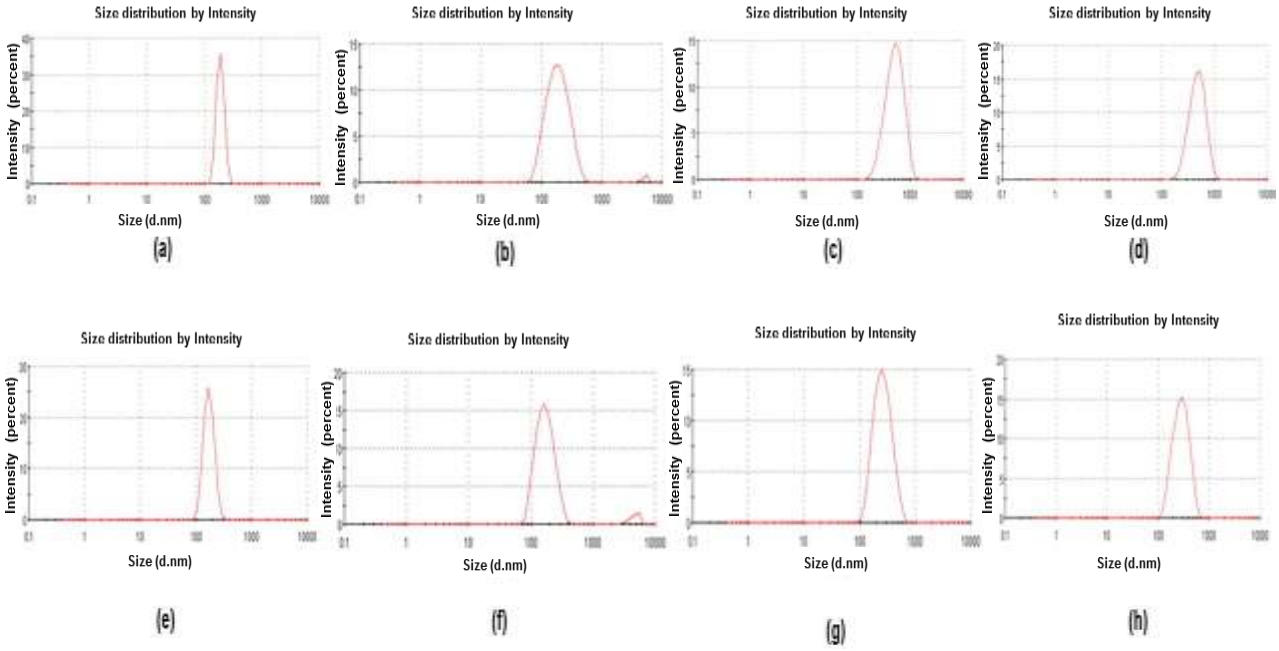


Figure S4. Measured DLS (a) **TR-A** in CH_3CN (mean size 189.8 nm). (b) **TR-A** at 50% water content (mean size of 200.4 nm). (c) **TR-A** at 60% water content (mean size 500.5 nm). (d) **TR-A** at 80% water content (mean size 541.8 nm). (e) **TR-B** in CH_3CN (mean size 173.1 nm). (f) **TR-B** at 60% water content (mean size 181.2 nm). (g) **TR-B** at 70% water content (mean size 273.1 nm). (h) **TR-B** at 90% water content (mean size 293.8 nm).

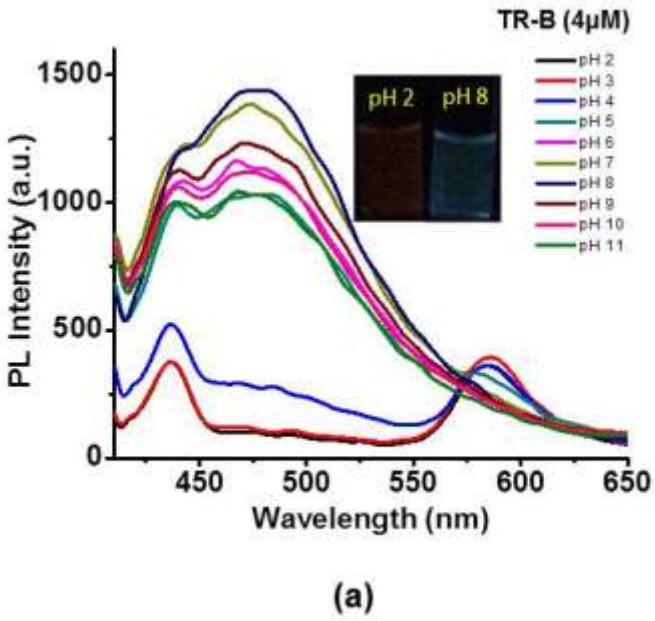


Figure S5. (a) Alterations in PL spectra of **TR-B** with different pH conditions from 2 to 11. Inset: photoimages of **TR-A** under UV lamp in acidic (pH = 2) and basic (pH = 8) conditions, with an excitation wavelength at λ_{ex} = 380 nm.

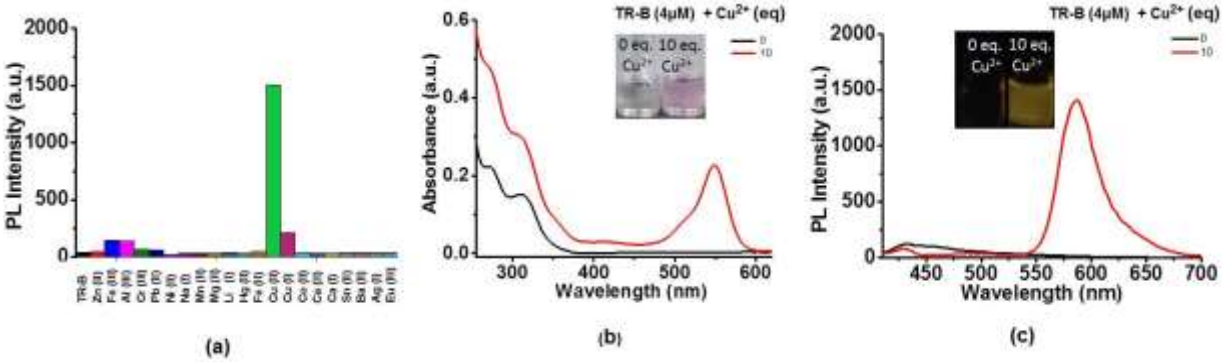


Figure S6. (a) Bar diagrams depicting PL intensity enhancement from RhB in **TR-B** with interactions of various metal ions. (b) UV-Vis spectral changes of **TR-B** in CH_3CN solution observed pink color as a result of interaction with Cu^{2+} metal ion. (c) PL spectral changes of **TR-B** in CH_3CN with the interaction of Cu^{2+} metal ion, Inset: photoimages of **TR-B** in the absence and presence of Cu^{2+} metal ion, with an excitation wavelength at λ_{ex} = 380 nm.

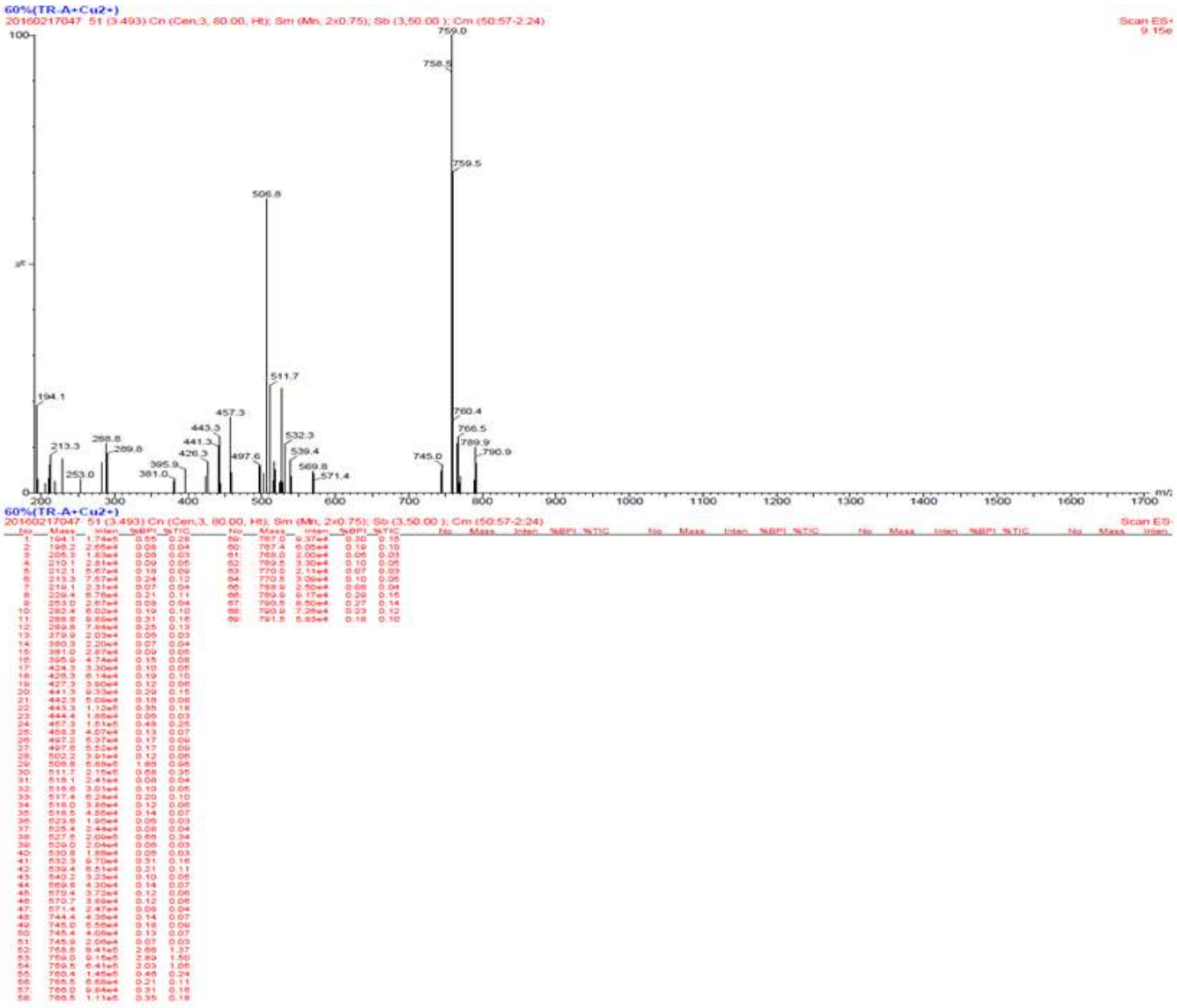


Figure S7. Mass spectrum of **TR-A** at 60% water content in the presence of Cu^{2+} metal ion.

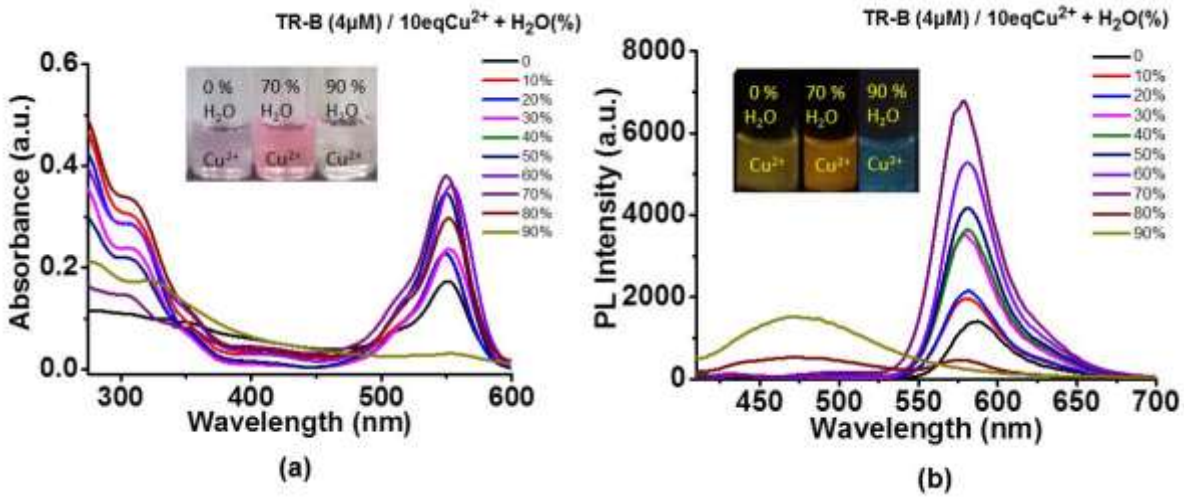


Figure S8. Upon the addition of Cu^{2+} (10 eq.) (a) UV-vis spectral changes (b) PL spectral changes of **TR-B** by increasing water fractions: 0, 10, 20, 30, 40, 50, 60, 70, and 80%, Insets: photoimages of **TR-B** in the presence of Cu^{2+} (at various water contents of 0, 70, and 90%) by naked eye observations and PL emissions, respectively, with a PL excitation wavelength at λ_{ex} = 380 nm.

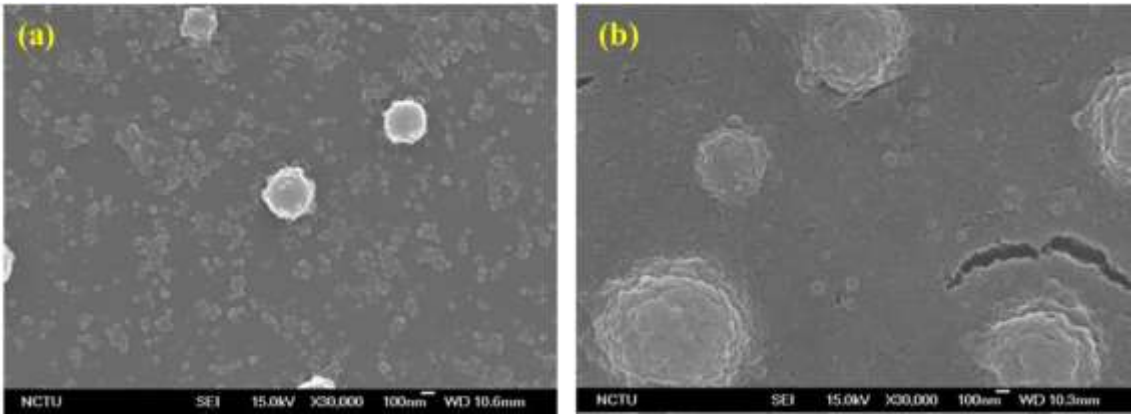


Figure S9. Morphological images of (a) **TR-A** at 50% water content in the prensence of Cu^{2+} (10eq.) (b) **TR-A** at 60% water content in the prensence of Cu^{2+} (10eq.).

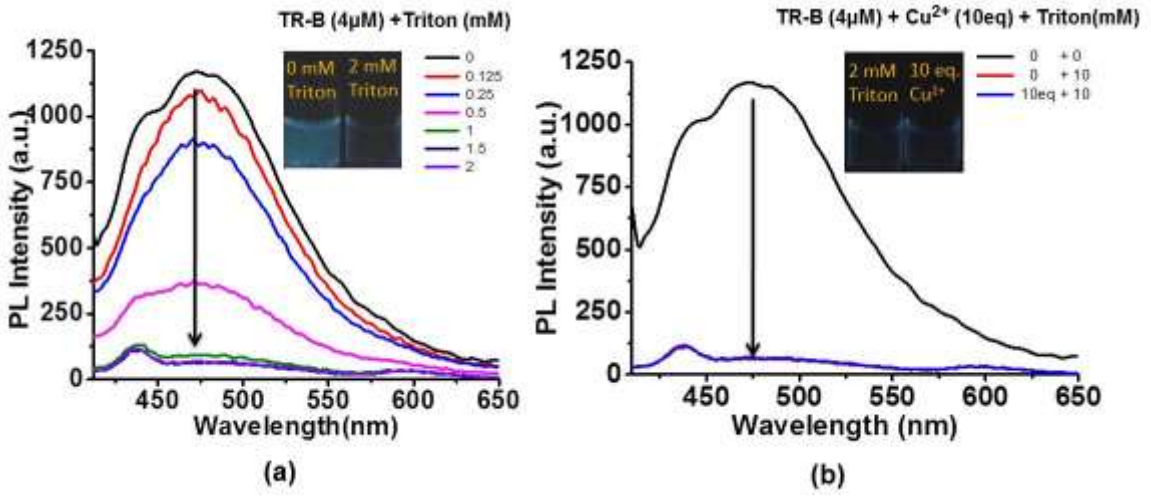


Figure S10. (a) PL spectra of **TR-B** at 90% water content in various triton-X-100 concentrations without Cu^{2+}. (b) PL spectra of **TR-B** at 90% water content in various triton-X-100 concentrations with Cu^{2+}, with a PL excitation wavelength at λ_{ex} = 380 nm.

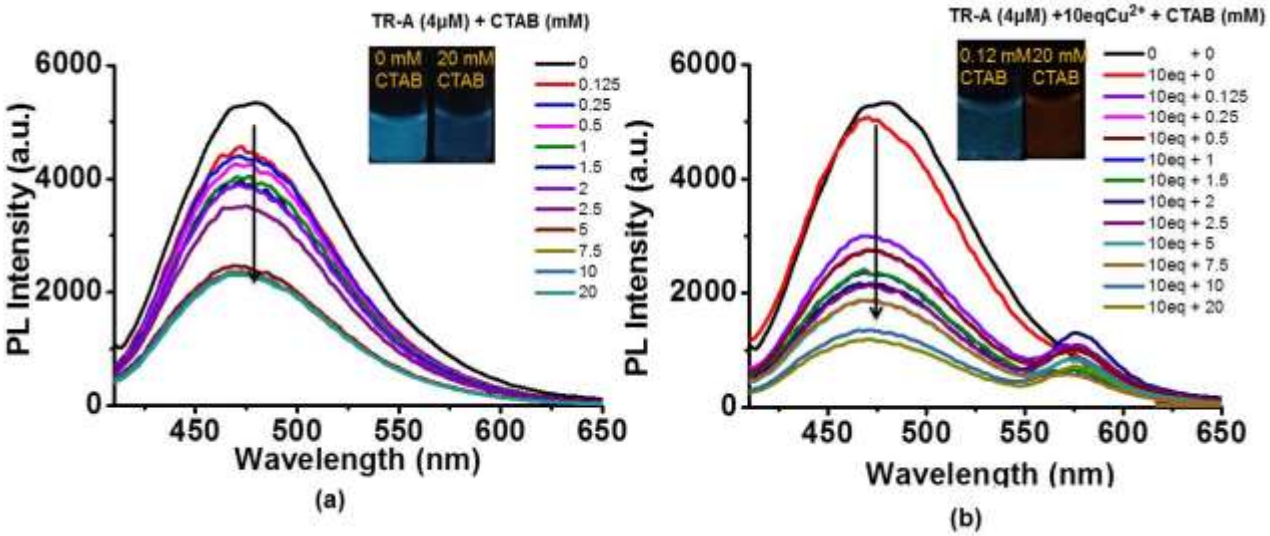


Figure S11. (a) PL spectra of **TR-A** at 80% water content in various CTAB concentrations without Cu^{2+}. (b) PL spectra of **TR-A** at 80% water content in various CTAB concentrations with Cu^{2+}, with a PL excitation wavelength at λ_{ex} = 380 nm.

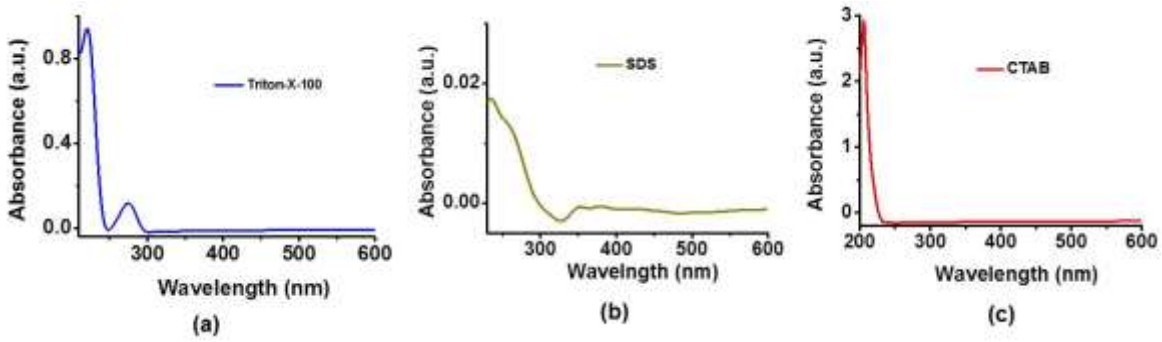


Figure S12. UV spectra of (a) Triton-X-100 at 80% water content (b) SDS at 80% water content (c) CTAB at 80% water content.

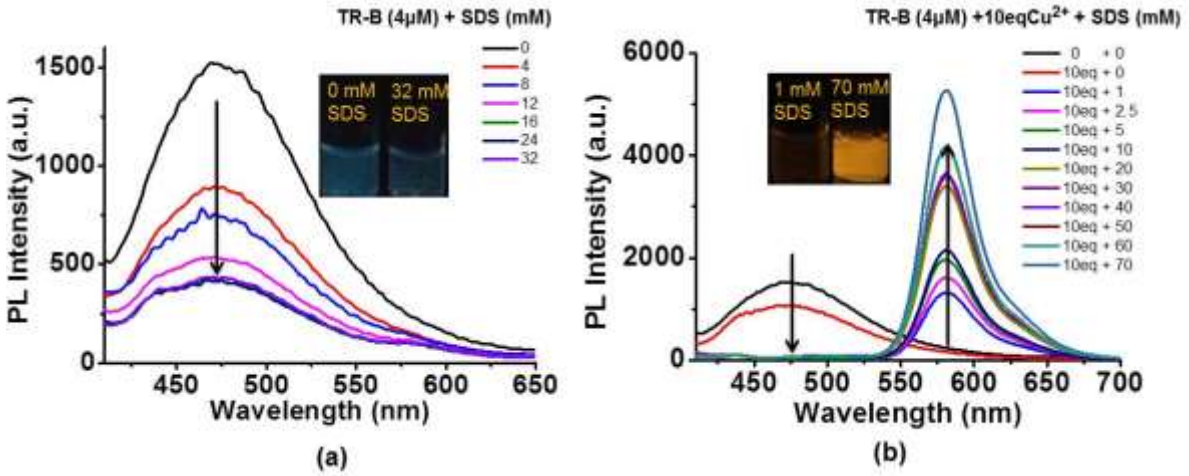


Figure S13. (a) PL spectra of **TR-B** at 90% water content in various SDS concentrations without Cu^{2+}. (b) PL spectra of **TR-B** at 90% water content in various SDS concentrations with Cu^{2+}, with a PL excitation wavelength at λ_{ex} = 380 nm.

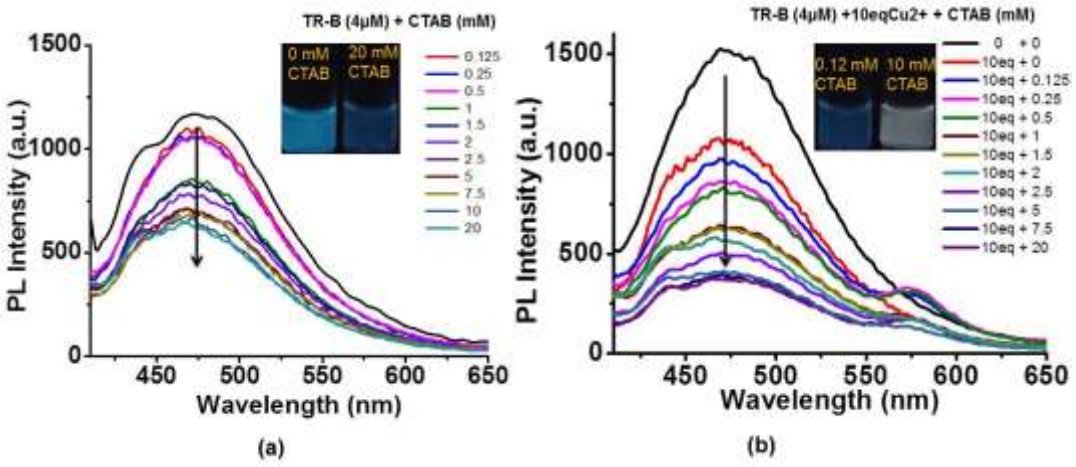


Figure S14. (a) PL spectra of **TR-B** at 90% water content in various CTAB concentrations without Cu^{2+}. (b) PL spectra of **TR-B** at 90% water content in various CTAB concentrations with Cu^{2+}, with a PL excitation wavelength at λ_{ex} = 380 nm.

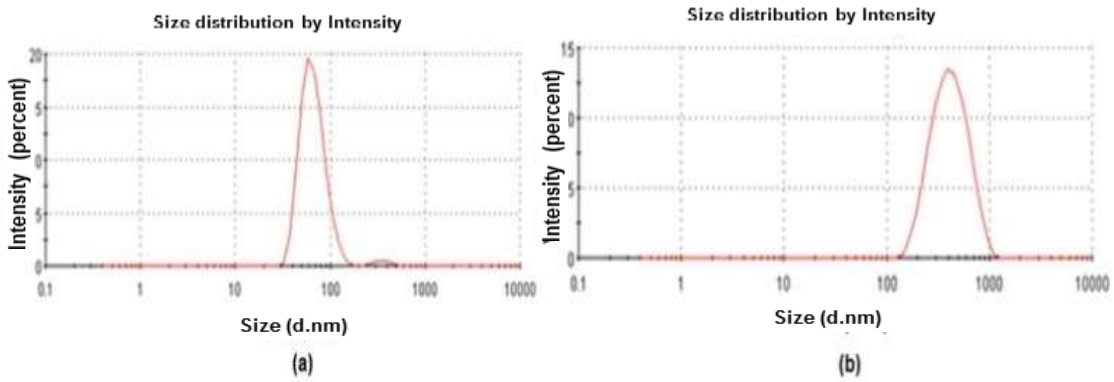


Figure 15. DLS spectra of (a) Triton-X-100 micelles at 80% water content (a mean size of 67.3 nm) (b) Triton-X-100 micelles at 80% water content in the presence of **TR-A** (a mean size of 435.5 nm).

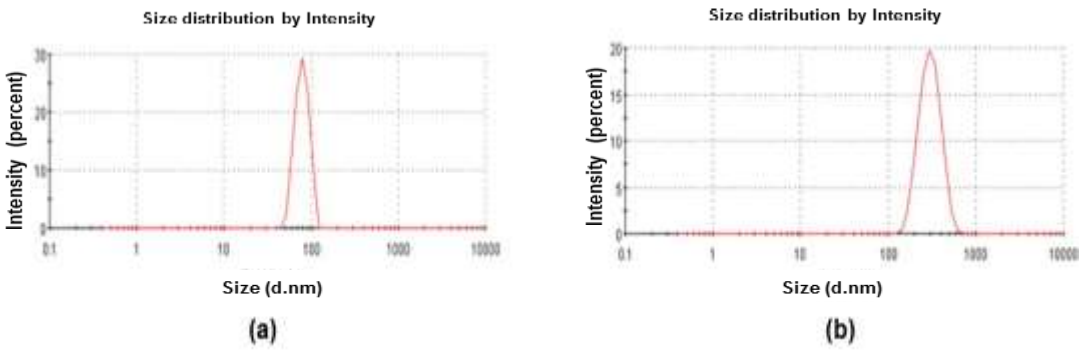


Figure S16. Measured DLS (a) Triton-X-100 micelles at 90% water content (mean size of 79.2 nm). (b) TriX100 micelles at 90% water content in the presence of **TR-B** (mean size of 309.1nm).

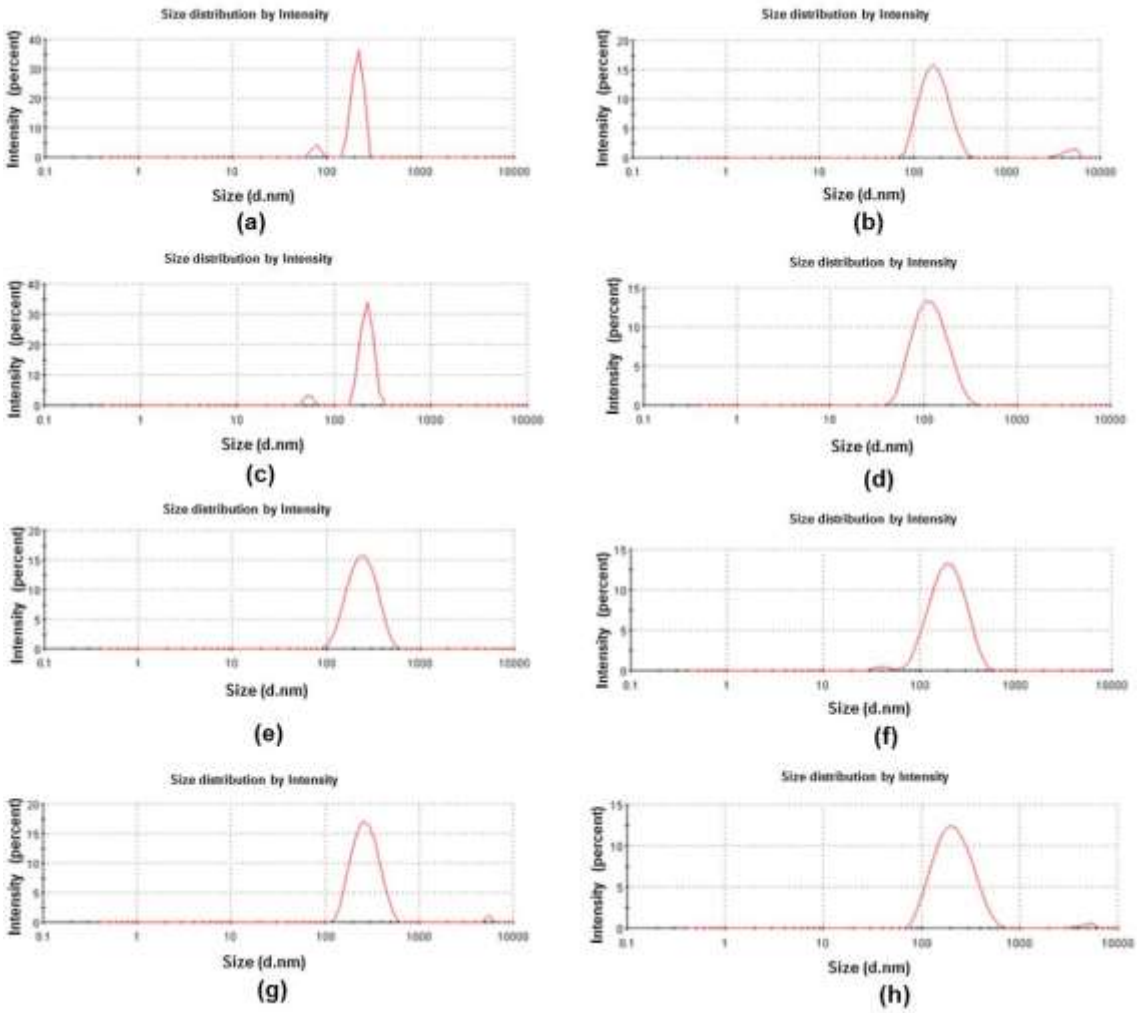


Figure S17. Measured DLS (a) SDS micelles at 80% water content (mean size of 216.1 nm). (b) SDS micelles at 80% water content in the presence of **TR-A** (mean size of 176.4 nm). (c) SDS micelles at 90% water content (mean size of 220.1 nm). (d) SDS micelles at 90% water content in the presence of **TR-B** (mean size of 126.3 nm). (e) CTAB micelles at 80% water content (mean size of 252.5 nm). (f) CTAB micelles at 80% water content in presence of **TR-A** (mean size of 211.2 nm). (g) CTAB micelles at 90% water content (mean size of 278.2 nm). (h) CTAB micelles at 90% water content in the presence of **TR-B** (mean size of 228.6 nm).

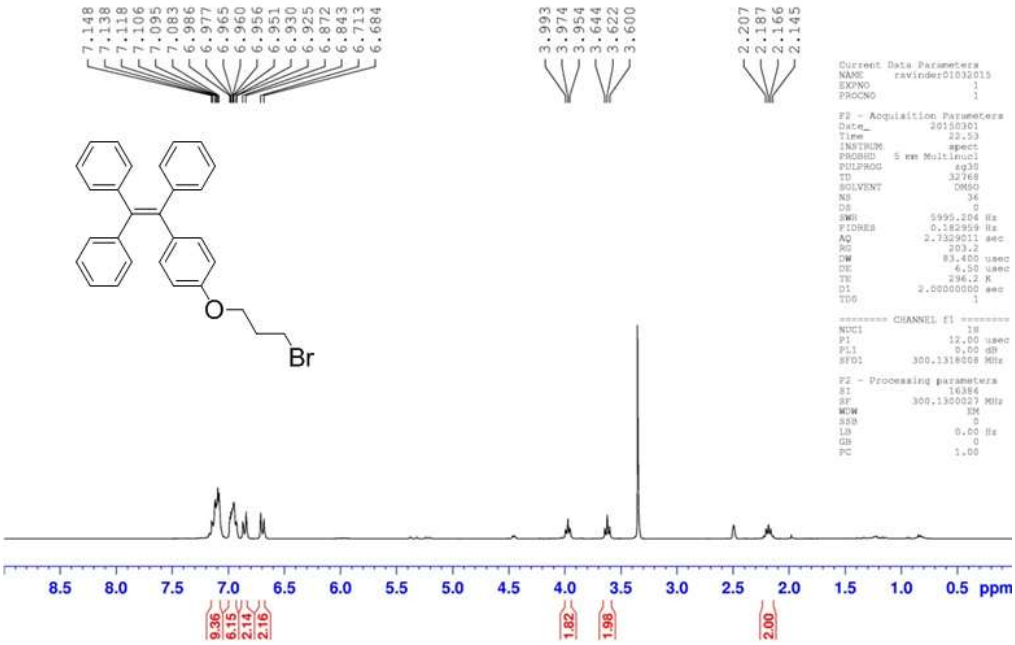


Figure S18. **1**. ^{1}H NMR of intermediate (**3**).

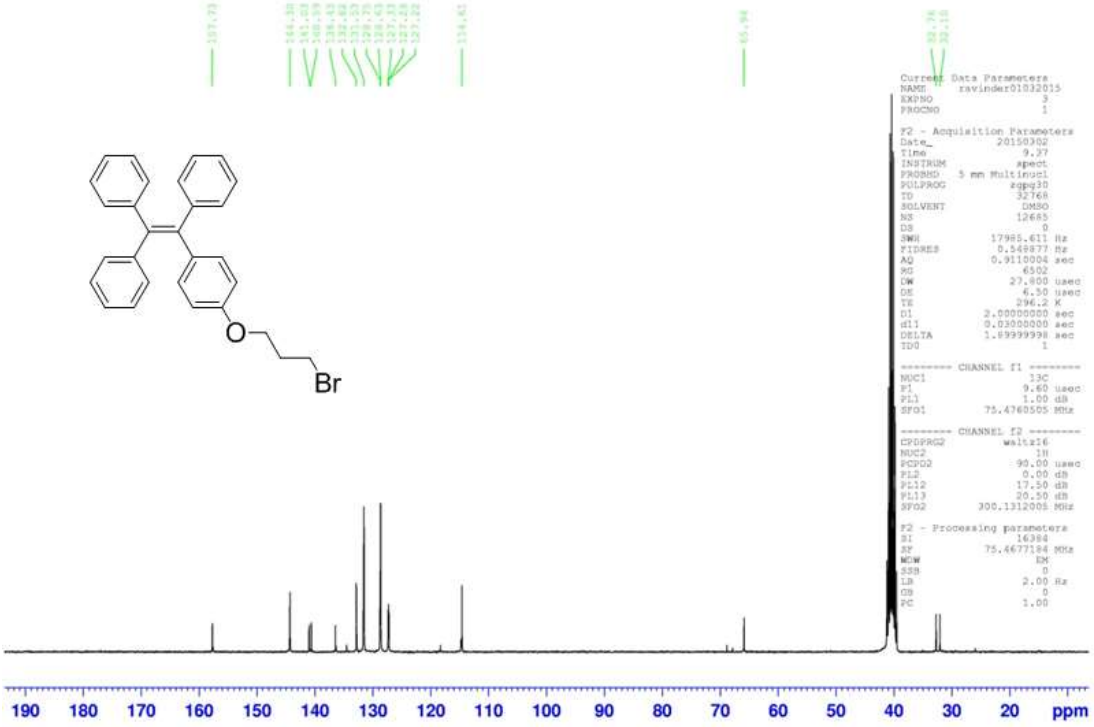


Figure S18.2. ^{13}C NMR of intermediate (3).

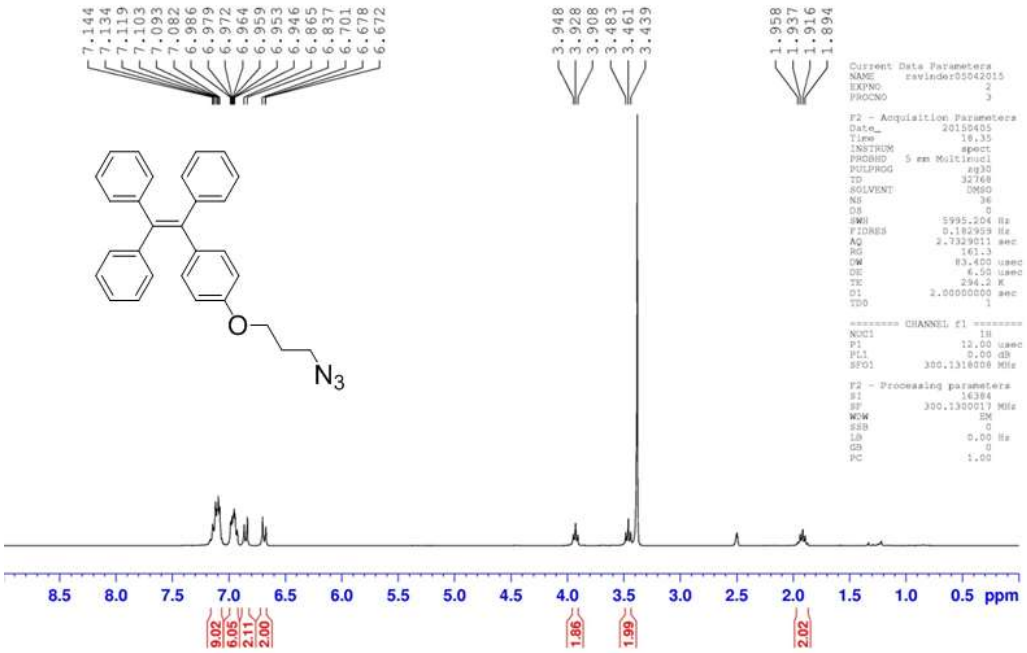


Figure S19.1. ^{1}H NMR of intermediate (4).

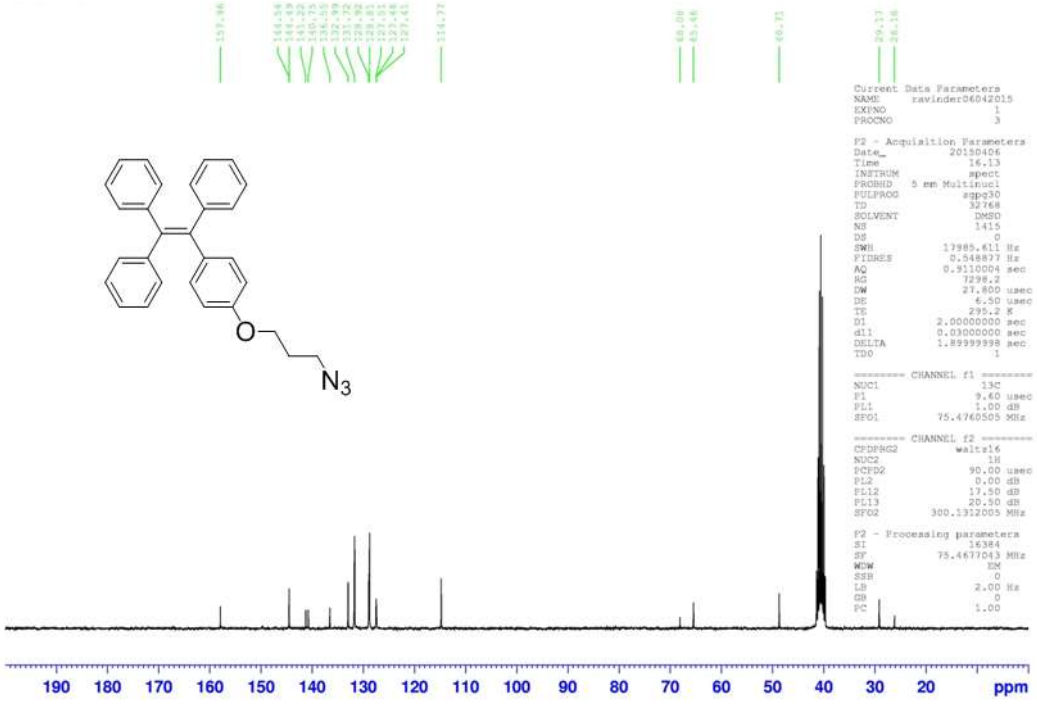


Figure S19.2. ^{13}C NMR of intermediate (4).

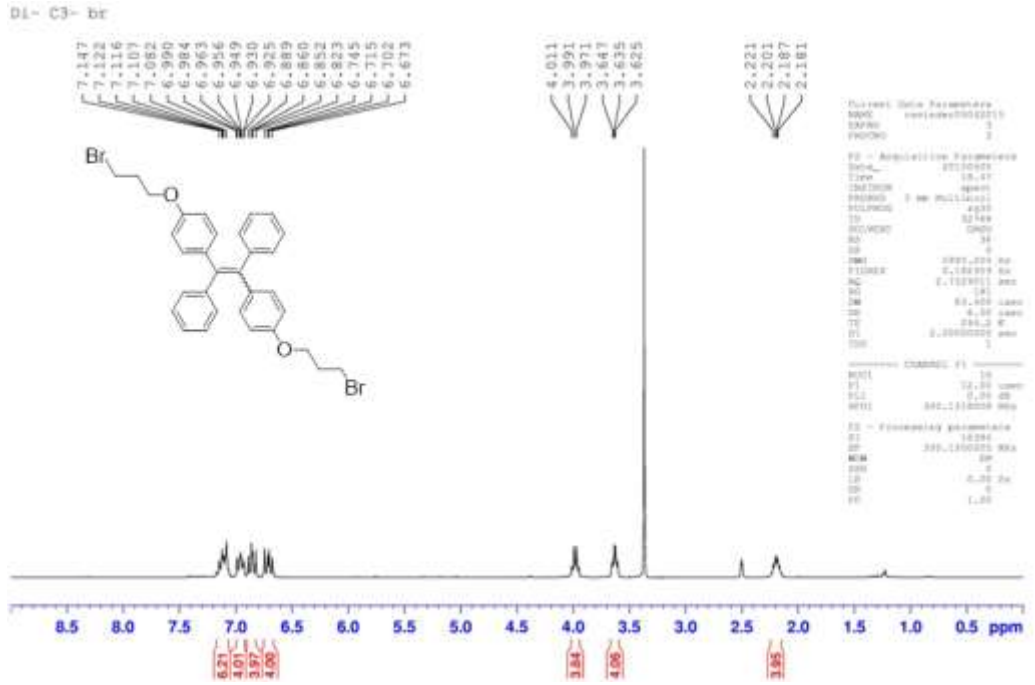


Figure S20.1. ^{1}H NMR of intermediate (5).

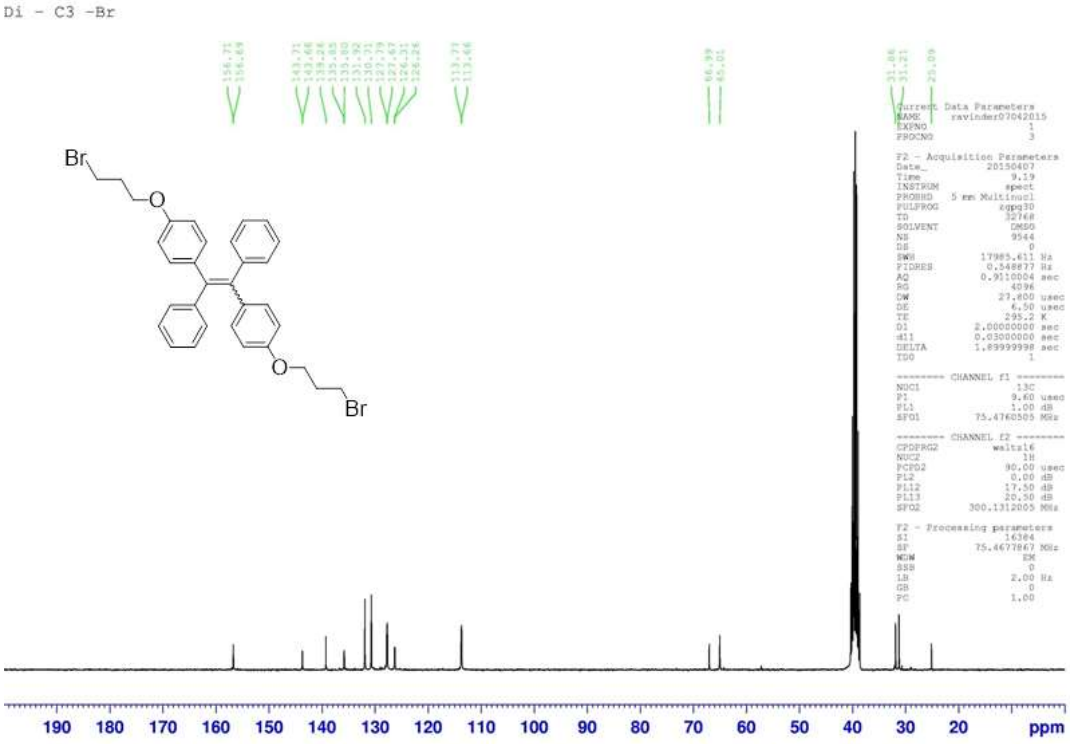


Figure S20.2. ^{13}C NMR of intermediate (5).

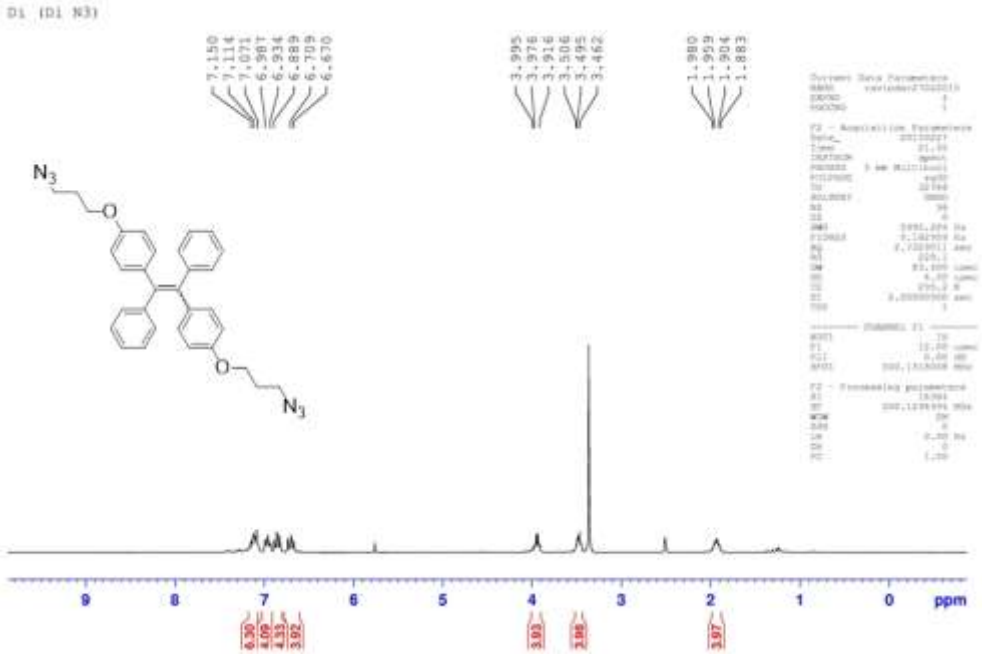


Figure S21.1. ^{1}H NMR of intermediate (6).

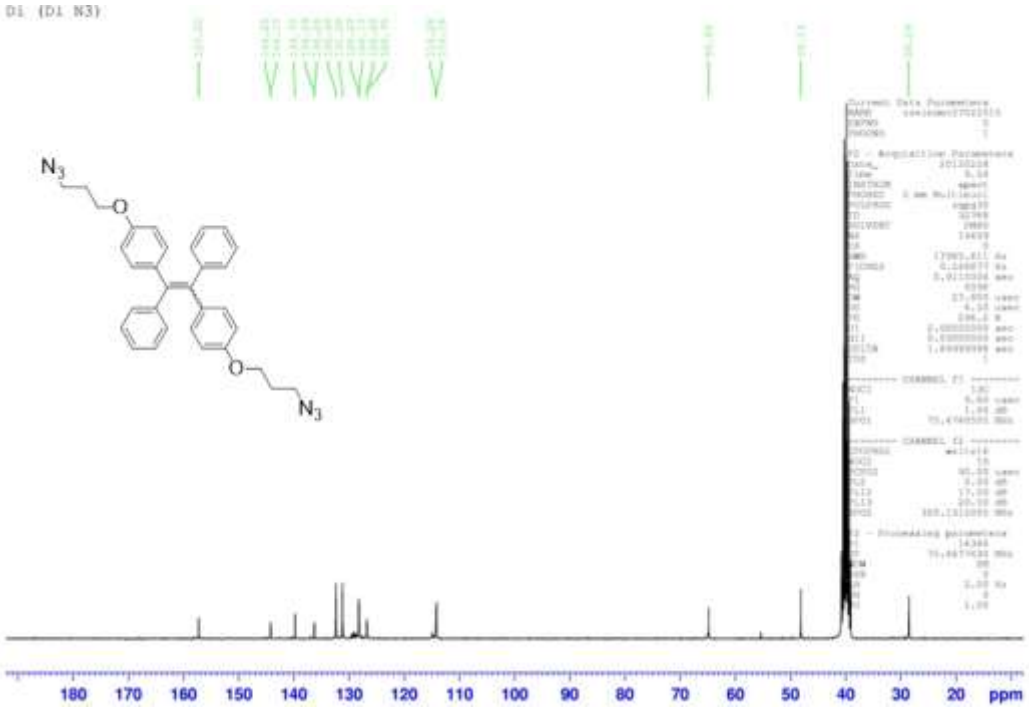


Figure S21.2. ^{13}C NMR of intermediate (6).

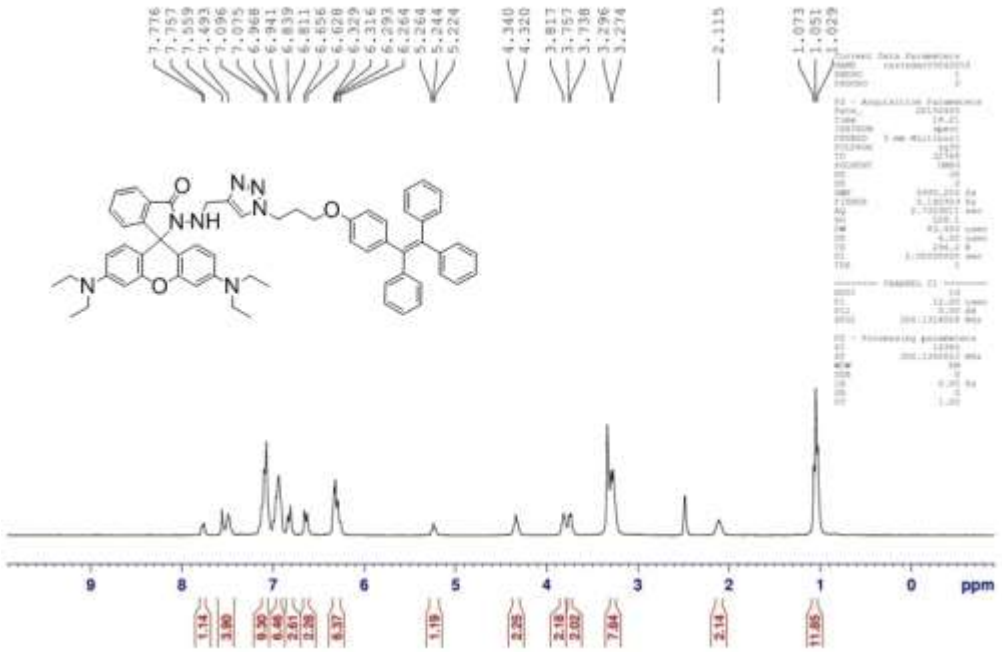


Figure S22.1. ^{1}H NMR of **TR-B**.

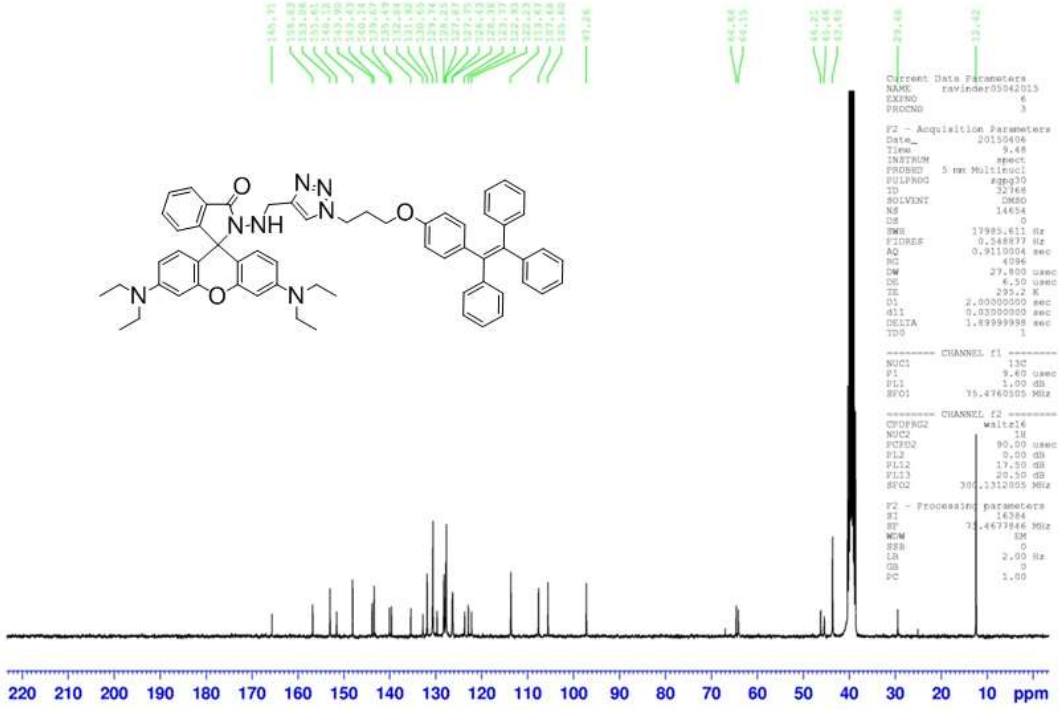


Figure S22.2. ^{13}C NMR of **TR-B**.

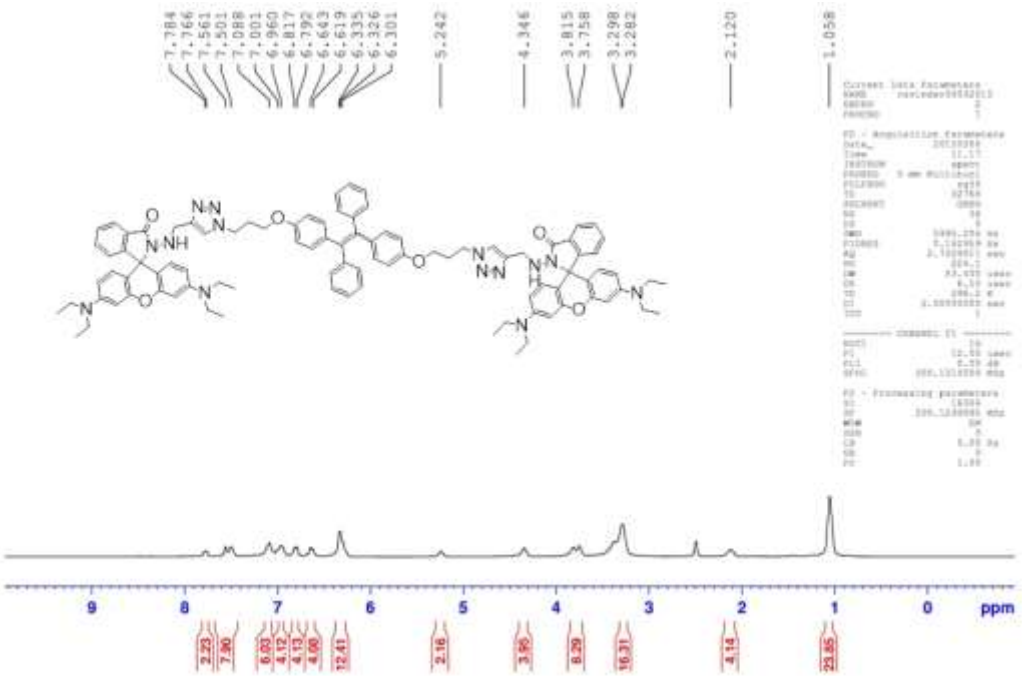


Figure S23.1. ^{1}H NMR of **TR-A**.

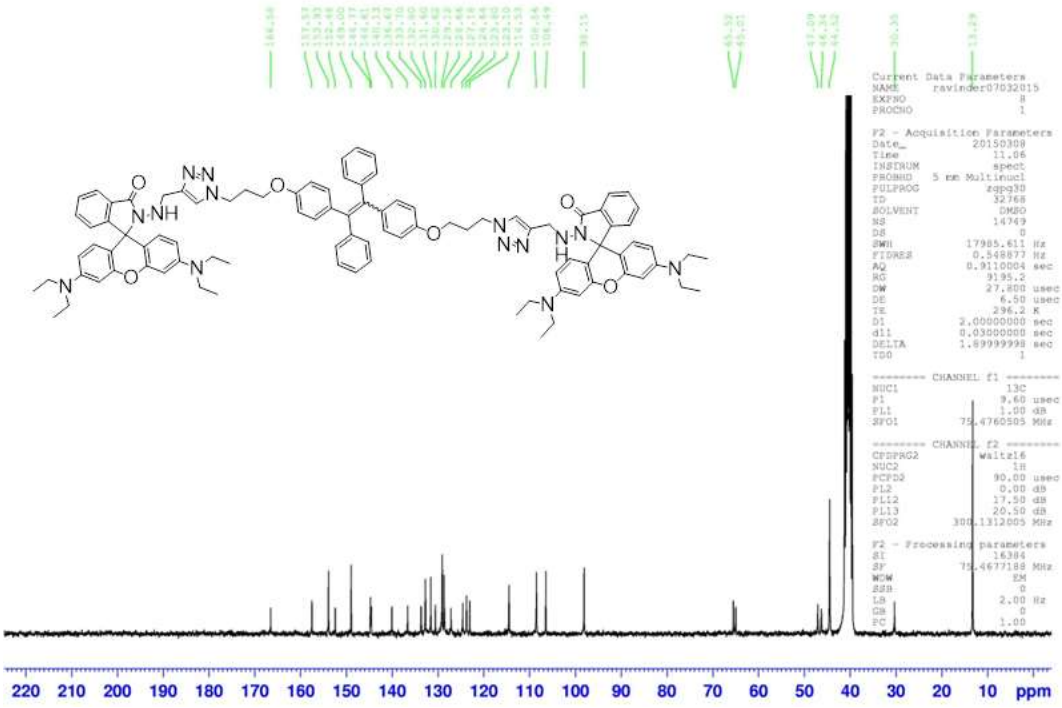


Figure S23.2. ^{13}C NMR of **TR-A**.

Department of Applied Chemistry, National Chiao Tung University

Elemental Analyzer Heraeus CHN-O Rapid Service Report

User Name: Ravinder Singh Department: Prof. H.C.Lin

Received Date: 20141223 Finished Date: 20141225

Experiment:

Sample Name:	MONO	MONO	DI-1ST	DI-1ST	DI-IIND	DI-IIND	
N%	10.47	10.51	12.46	12.64	12.75	12.62	
C%	78.15	77.79	73.28	73.51	73.48	73.67	
H%	6.44	6.55	6.64	6.60	6.48	6.44	

Sample Name:							
N%							
C%							
H%							

Estimate:

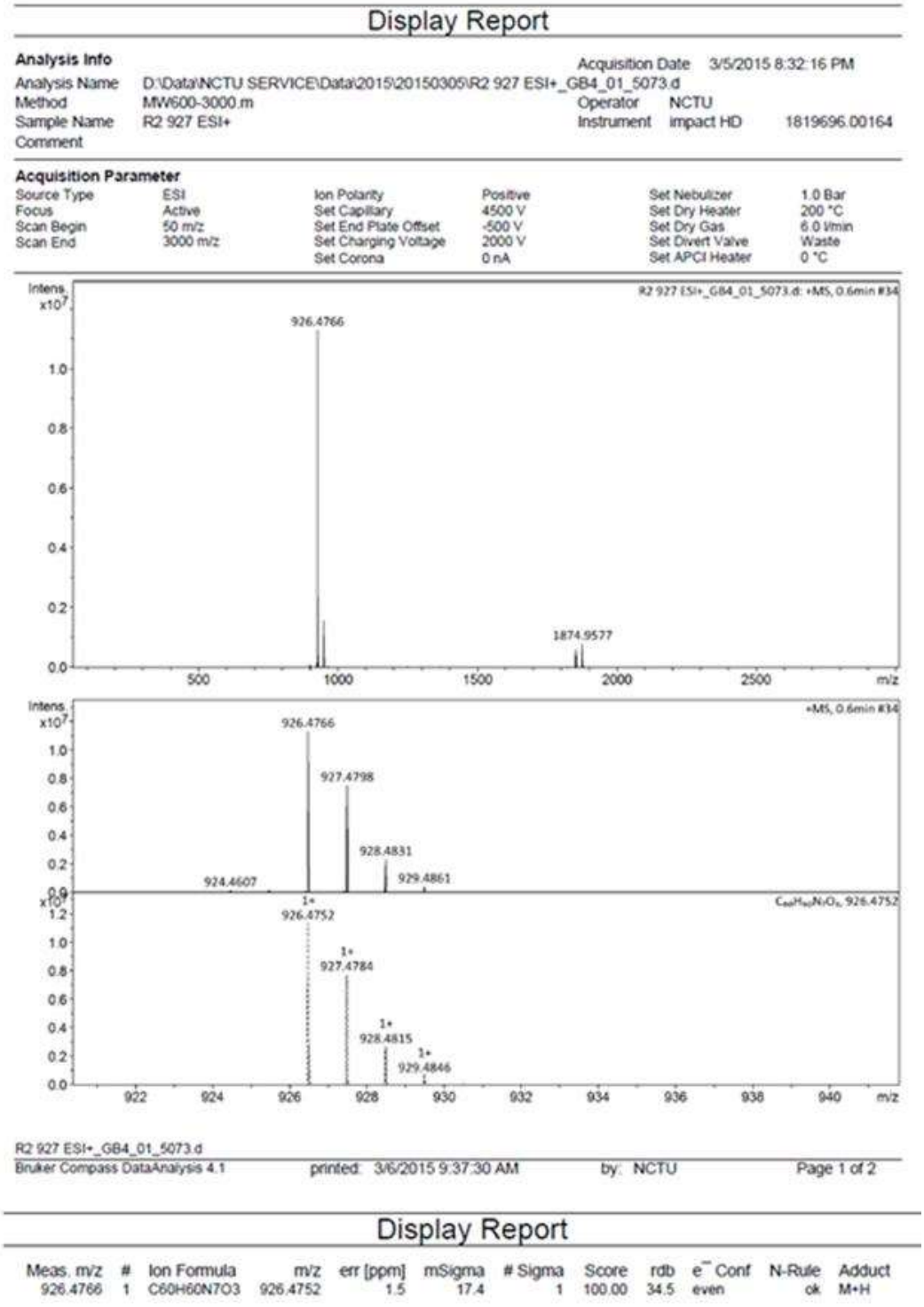
Sample Name:	MONO	DI-1ST	DI-IIND				
N%	10.59	12.90	12.90				
C%	77.81	74.28	74.28				
H%	6.42	6.50	6.50				

Standard： Acetanilide

Remarks:

Equipment Manager Signature: 謝有容 Technician Signature: 技士李蘊明

Figure S24. Elementary analysis data of **TR-A** and **TR-B**.



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
926.4766	1	C60H60N7O3	926.4752	1.5	17.4	1	100.00	34.5	even	ok	M+H

Figure S25. HRMS (ESI) spectrum of **TR-B**.

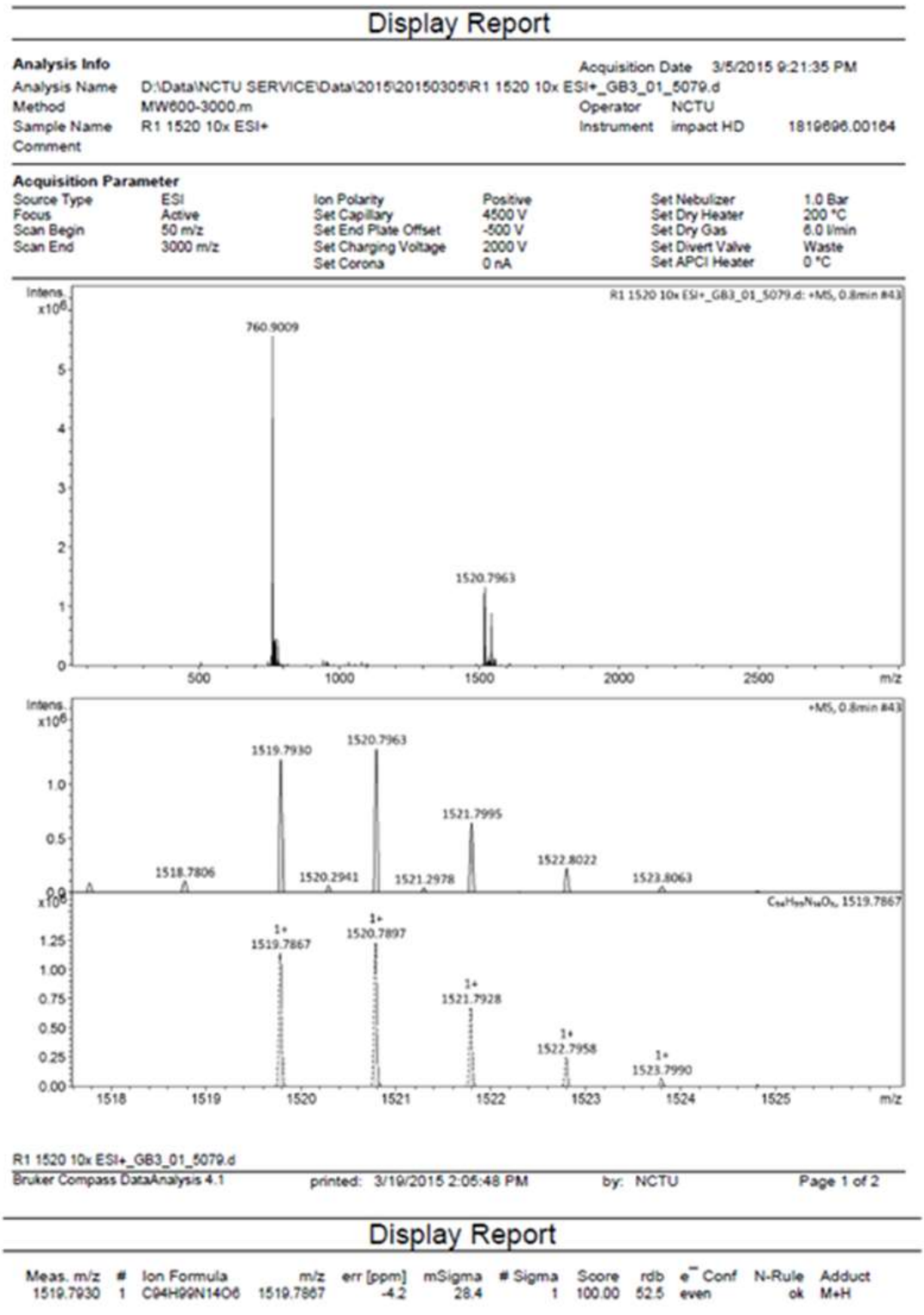


Figure S26. HRMS (ESI) spectrum of **TR-A**.

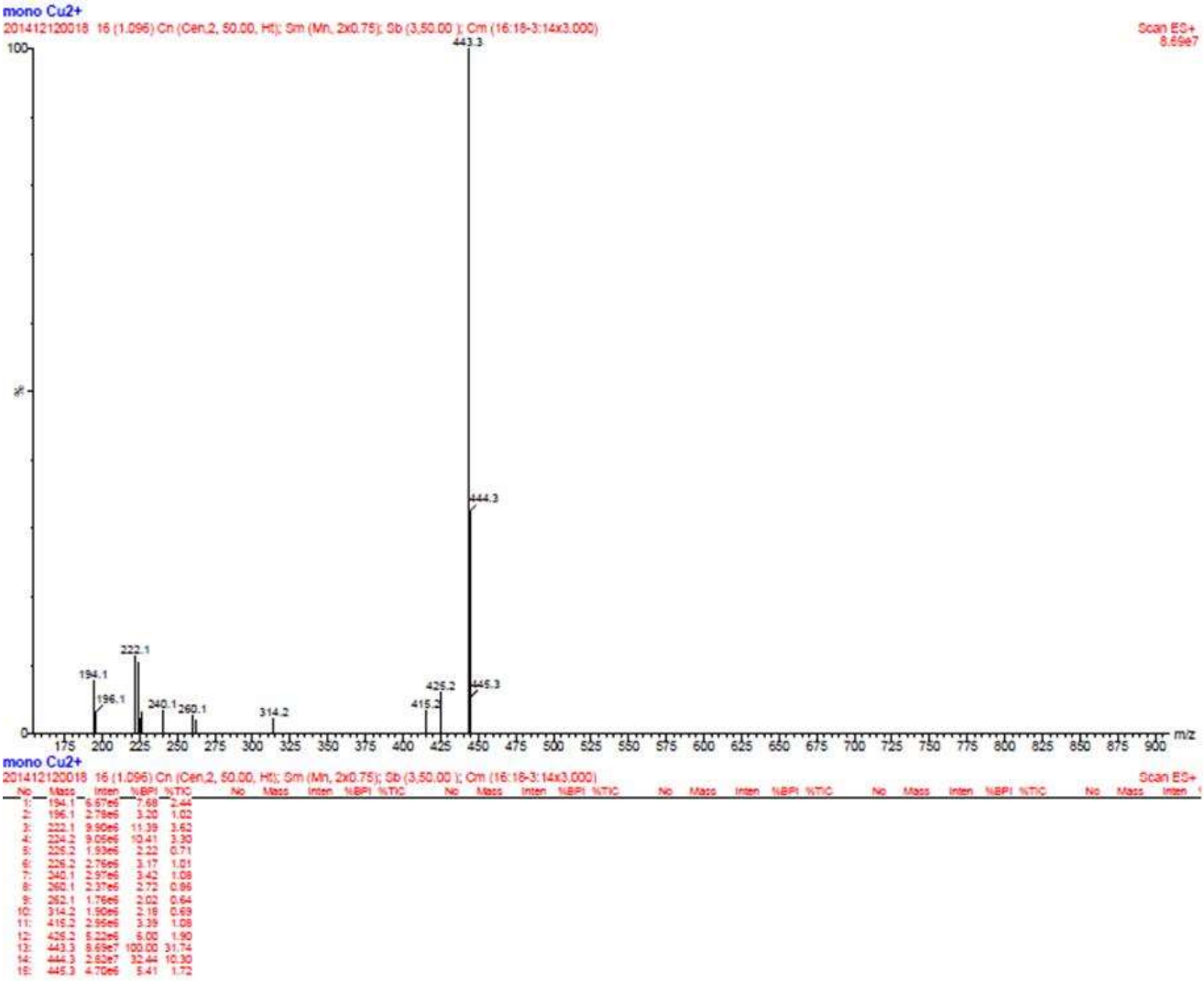


Figure S27. Mass spectrum of **TR-B** in the presence of Cu^{2+} metal ion.

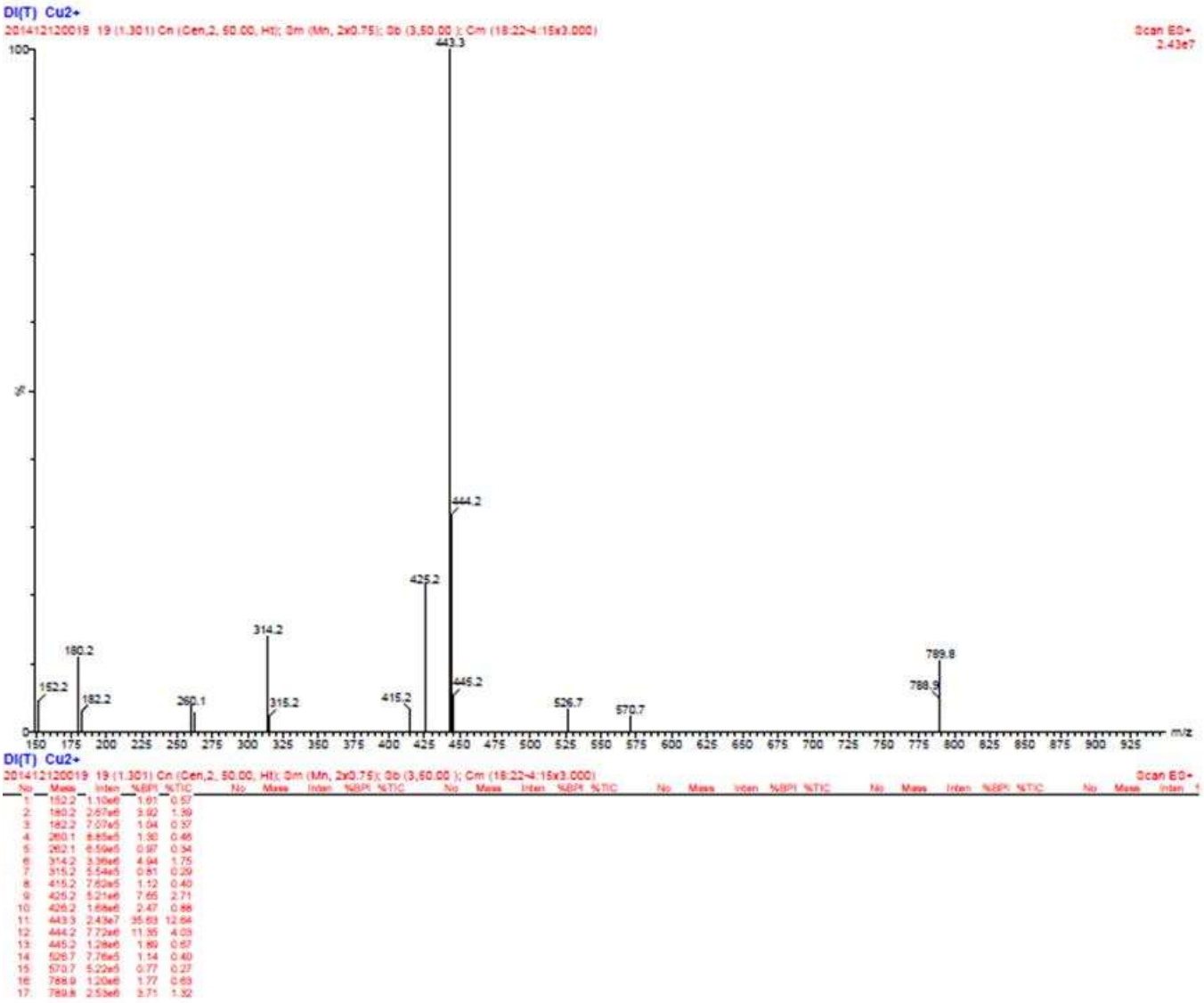


Figure S28. Mass spectrum of **TR-A** in the presence of Cu^{2+} metal ion.