

Supporting Information

for

**A fully dynamic five-component triangle via
self-sorting**

Michael Schmittel, Kingsuk Mahata,*

*Center of Micro and Nanochemistry and Engineering, Organische Chemie I, Universität
Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany,
E-mail: schmittel@chemie.uni-siegen.de
Fax: (+49) 271-740-3270*

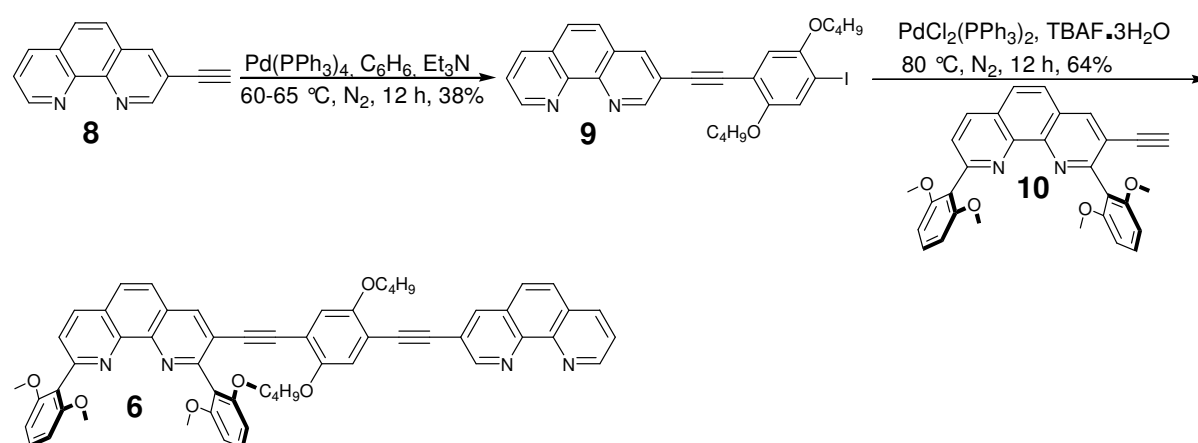
Table of Contents

1	General	S2
2	Synthesis	S2
3	¹ H and ¹³ C spectra	S6
4	ESI-MS spectra	S9
5	DOSY	S12
6	DPV	S13
7	References	S14

General

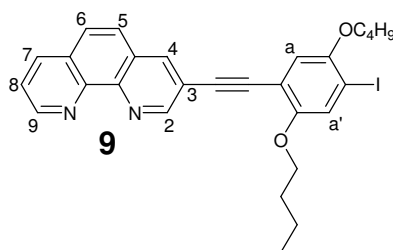
All commercial reagents were used without further purification. The solvents were dried with appropriate desiccants and distilled prior to use. Silica gel (60-230 mesh) was used for column chromatography. ^1H NMR and ^{13}C NMR were recorded on a Bruker Avance 400 MHz spectrometer using the deuterated solvent as the lock and residual solvent as the internal reference. The following abbreviations were utilised to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublet and m = multiplet. The numbering of the carbon atoms of the molecular formulae shown in the experimental section is only used for the assignments of the NMR signal and is not in accordance with the IUPAC nomenclature rules. Electrospray ionisation mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca. Differential pulse voltammetry (DPV) was measured on a Parstat 2273 in dry acetonitrile with 0.1 M $n\text{Bu}_4\text{NPF}_6$ as electrolyte. Melting points were measured on a Büchi SMP-20 and are uncorrected. Infrared spectra were recorded using a Varian 1000 FT-IR instrument. Elemental analysis measurements were done using a EA 3000 CHNS. Compound **5**, 1 **7**² and precursors for **6** (**8** and **10**²) were synthesised according to known procedures.

Synthesis



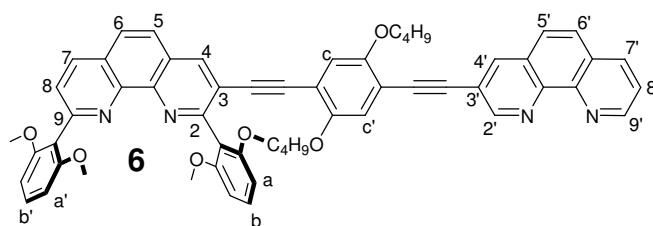
Scheme S1. Synthesis of ligand **6**.

Synthesis of **9**



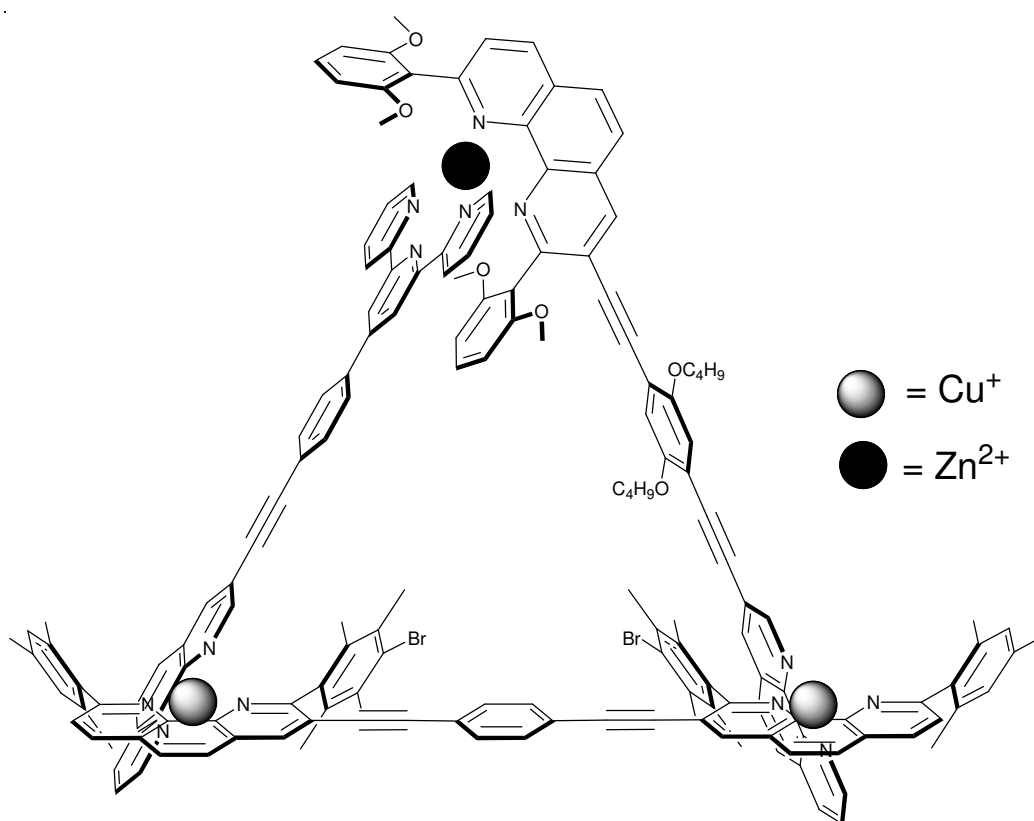
Into an oven-dried 250 mL three-neck round-bottom flask, equipped with reflux condenser and stir bar was added 3-ethynyl-[1,10]phenanthroline (**8**; 300 mg, 1.47 mmol), 1,4-dibutoxy-2,5-diiodobenzene (3.48 g, 7.34 mmol) and Pd(PPh₃)₄ (51.0 mg, 44.1 μmol) under N₂ atmosphere. After addition of dry benzene (70 mL) and triethylamine (30 mL), the reaction mixture was stirred at 60-65 °C for 12 h. The reaction vessel was cooled down and the solvents were evaporated to dryness. The resulting crude solid was then dissolved in dichloromethane (200 mL) and washed successively with aq. KOH (200 mL) and water (200 mL). After drying over Na₂SO₄, solvent was removed under reduced pressure. The crude product was purified using column chromatography (SiO₂). For a first separation dichloromethane was used as eluent. Finally, the target compound was furnished using a 1:4 mixture of ethyl acetate and dichloromethane. Yield 38%; mp 122°C; ¹H NMR (400 MHz, CDCl₃) δ 1.01 (t, ³J = 7.4 Hz, 3 H, CH₃), 1.03 (t, ³J = 7.4 Hz, 3 H, CH₃), 1.52-1.66 (m, 4 H, CH₂), 1.80-1.90 (m, 4 H, CH₂), 4.02 (t, ³J = 6.4 Hz, 2 H, OCH₂), 4.05 (t, ³J = 6.4 Hz, 2 H, OCH₂), 6.99 (s, 1 H, a-H), 7.36 (s, 1 H, a'-H), 7.65 (dd, ³J = 8.0 Hz, ³J = 4.4 Hz, 1 H, 8-H), 7.77 (d, ³J = 8.8 Hz, 1 H, 6-H), 7.83 (d, ³J = 8.8 Hz, 1 H, 5-H), 8.26 (dd, ³J = 8.0 Hz, ⁴J = 1.6 Hz, 1 H, 7-H), 8.36 (d, ⁴J = 2.0 Hz, 1 H, 4-H), 9.21 (dd, ³J = 4.4 Hz, ⁴J = 1.6 Hz, 1 H, 9-H), 9.28 (d, ⁴J = 2.0 Hz, 1 H, 2-H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (2C), 19.3, 19.4, 31.3 (2C), 69.6, 69.8, 88.7, 90.0, 91.1, 112.7, 115.8, 119.8, 123.2, 123.8, 126.1, 127.3, 127.8, 128.9, 136.0, 137.8, 144.7, 146.0, 150.7, 151.9, 152.2, 154.6; IR (KBr) ν 2931, 2871, 2212, 1612, 1594, 1585, 1554, 1493, 1464, 1442, 1430, 1420, 1378, 1346, 1325, 1292, 1274, 1263, 1237, 1213, 1143, 1123, 1097, 1066, 1042, 1025, 1014, 1004, 991, 976, 940, 912, 896, 856, 839, 826, 819, 807, 780, 767, 736, 729, 707, 665; ESI-MS *m/z* (%) 551.2 (100) [M + H]⁺. Anal. Calcd for C₂₈H₂₇IN₂O₂: C, 61.10; H, 4.94; N, 5.09. Found: C, 60.95; H, 4.88; N, 5.04.

Synthesis of **6**



Compound **10** (160 mg, 336 μmol), **9** (185 mg, 336 μmol), TBAF \cdot 3H₂O (636 mg, 2.02 mmol), and PdCl₂(PPh₃)₂ (7.50 mg, 11.0 μmol) were combined in a Schlenk flask under nitrogen atmosphere. The solid mixture was stirred at 80 °C for 12 h. Then, it was cooled, dissolved with dichloromethane, and washed successively with aqueous KOH (200 mL) and water (5 \times 200 mL). After drying over Na₂SO₄, the organic solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO₂; CH₂Cl₂/EtOAc, 9:1) furnishing **6** as a yellow solid. Yield 64%; mp 250-252 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.06 (t, ³J = 7.6 Hz, 3 H, CH₃), 1.08 (t, ³J = 7.6 Hz, 3 H, CH₃), 1.54-1.69 (m, 4 H, CH₂), 1.80-1.92 (m, 4 H, CH₂), 3.71 (s, 6 H, OCH₃), 3.74 (s, 6 H, OCH₃), 3.96 (t, ³J = 6.4 Hz, 2 H, OCH₂), 4.02 (t, ³J = 6.4 Hz, 2 H, OCH₂), 6.41 (s, 1 H, c-H), 6.66 (d, ³J = 8.4 Hz, 2 H, [a/a']-H), 6.67 (d, ³J = 8.4 Hz, 2 H, [a/a']-H), 7.03 (s, 1 H, c'-H), 7.30 (t, ³J = 8.4 Hz, 1 H, [b/b']-H), 7.33 (t, ³J = 8.4 Hz, 1 H, [b/b']-H), 7.63 (d, ³J = 8.0 Hz, 1 H, 8-H), 7.65 (dd, ³J = 8.0 Hz, ³J = 4.0 Hz, 1 H, 8'-H), 7.77 (d, ³J = 8.8 Hz, 1 H, [6/6']-H), 7.79 (d, ³J = 8.8 Hz, 1 H, [6/6']-H), 7.83 (d, ³J = 8.8 Hz, 2 H, [5,5']-H), 8.23 (d, ³J = 8.0 Hz, 1 H, 7-H), 8.26 (dd, ³J = 8.0 Hz, ⁴J = 1.6 Hz, 1 H, 7'-H), 8.35 (d, ⁴J = 2.0 Hz, 1 H, 4'-H), 8.41 (s, 1 H, 4-H), 9.21 (dd, ³J = 4.0 Hz, ⁴J = 1.6 Hz, 1 H, 9'-H), 9.27 (d, ⁴J = 2.0 Hz, 1 H, 2'-H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0 (2C), 19.3, 19.4, 31.3, 31.4, 56.3, 56.5, 69.2, 69.5, 90.4, 90.6, 91.8, 93.5, 104.5, 105.2 (2C), 112.9, 115.0, 117.2, 117.3, 119.9, 120.8, 123.2, 125.8, 126.1, 126.2, 127.0, 127.2, 127.3, 127.8, 128.0, 128.9, 129.6, 129.8, 135.3, 136.0, 137.8, 138.1, 144.7, 145.1, 146.0, 146.1, 150.7, 152.2, 153.1, 153.8, 155.3, 156.8, 158.6, 158.9; IR (KBr) ν 3416, 2956, 2934, 2871, 2836, 2361, 2338, 2208, 1617, 1598, 1590, 1559, 1540, 1498, 1473, 1458, 1432, 1423, 1410, 1396, 1303, 1277, 1251, 1213, 1174, 1142, 1110, 1062, 1022, 991, 909, 891, 842, 781, 766, 732; ESI-MS *m/z* (%) 899.5 (100) [M + H]⁺. Anal. Calcd for C₅₈H₅₀N₄O₆ \cdot H₂O: C, 75.96; H, 5.72; N, 6.11. Found: C, 76.34; H, 5.57; N, 6.14.

Synthesis of isosceles triangle T



A mixture of **5** (4.02 mg, 3.52 μmol), **6** (3.17 mg, 3.52 μmol), **7** (1.80 mg, 3.52 μmol), Zn(OTf)₂ (1.28 mg, 3.52 μmol) and [Cu(MeCN)₄]PF₆ (2.63 mg, 7.05 μmol) were refluxed in a mixture of dichloromethane (10 mL) and acetonitrile (30 mL) for 3 h. The solvents were evaporated under reduced pressure and the solid was characterised as such. Yield quantitative; mp > 260 °C; IR (KBr) ν 3448, 3069, 2953, 2933, 2870, 2211, 1617, 1602, 1589, 1550, 1499, 1475, 1427, 1406, 1384, 1277, 1256, 1224, 1161, 1112, 1069, 1030, 1019, 989, 912, 843, 791, 768, 725, 638; ESI-MS m/z (%) 685.8 (65) [M - 2PF₆ - 2OTf]⁴⁺, 963.7 (100) [M - 2PF₆ - OTf]³⁺, 1519.5 (10) [M - 2PF₆]²⁺. Anal. Calcd for C₁₆₁H₁₂₇Br₂Cu₂F₁₈N₁₃O₁₂P₂S₂Zn•3CH₂Cl₂ C, 56.92; H, 3.85; N, 5.08; S, 1.79. Found: C, 56.87; H, 3.30; N, 5.20; S, 2.06.

NMR Spectra

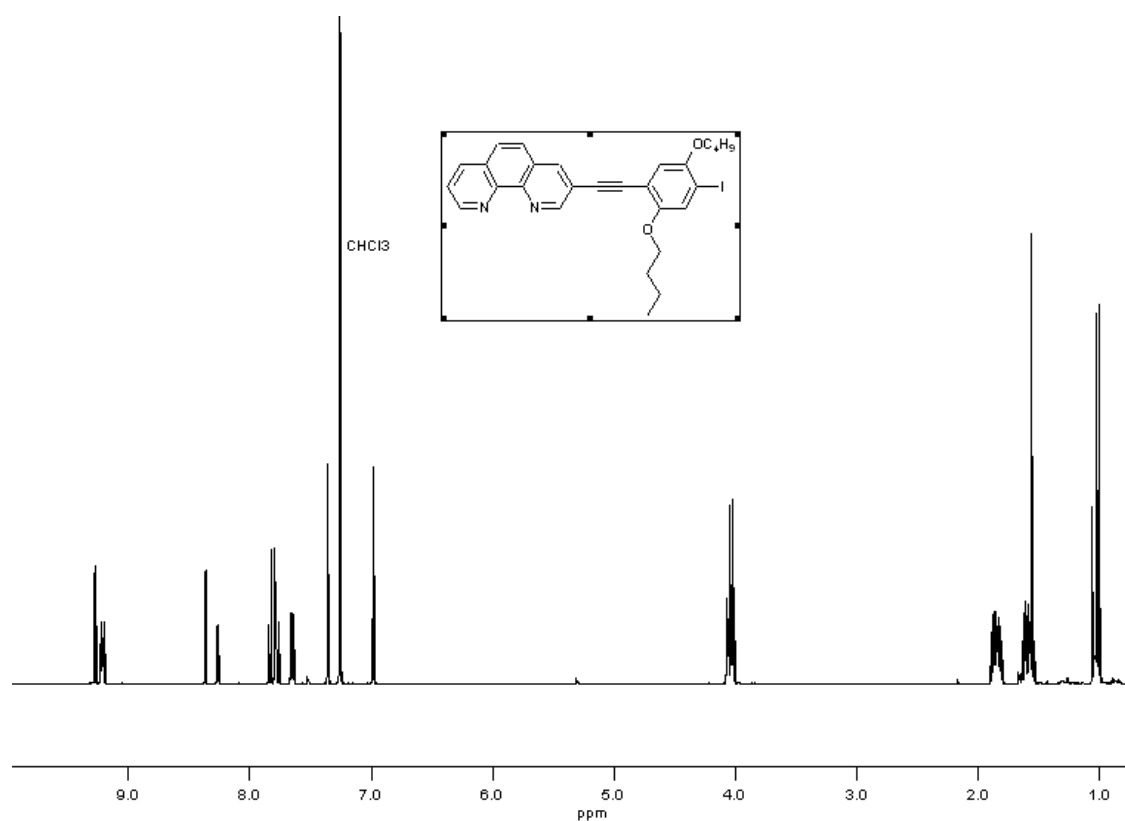


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **9**.

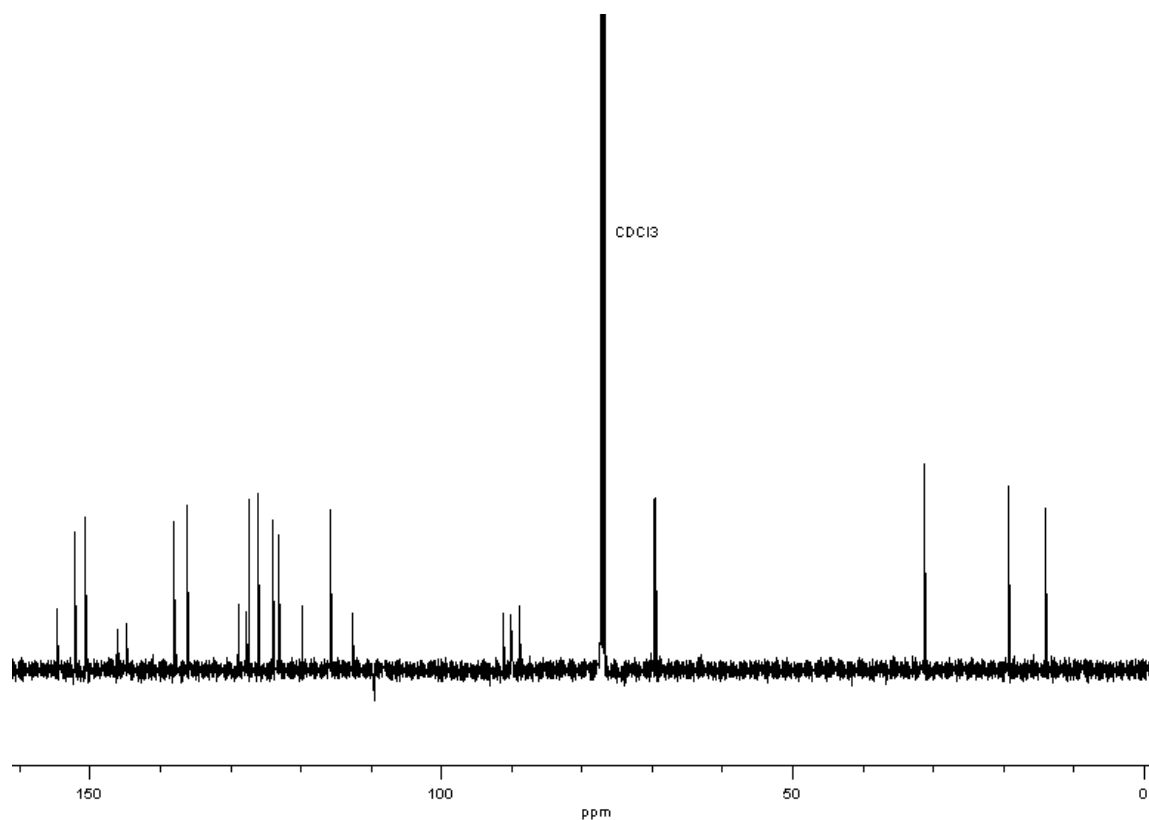


Figure S2. ¹³C NMR spectrum (100 MHz, CDCl₃, 298 K) of **9**.

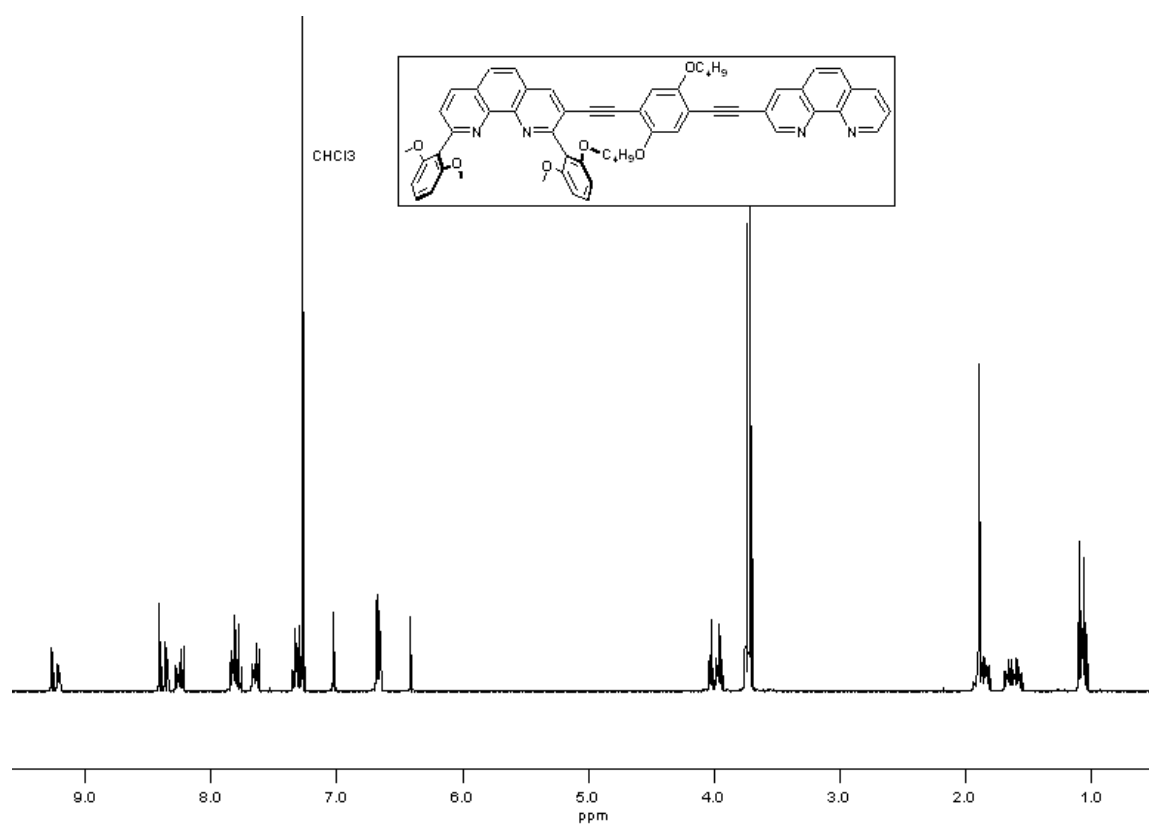


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **6**.

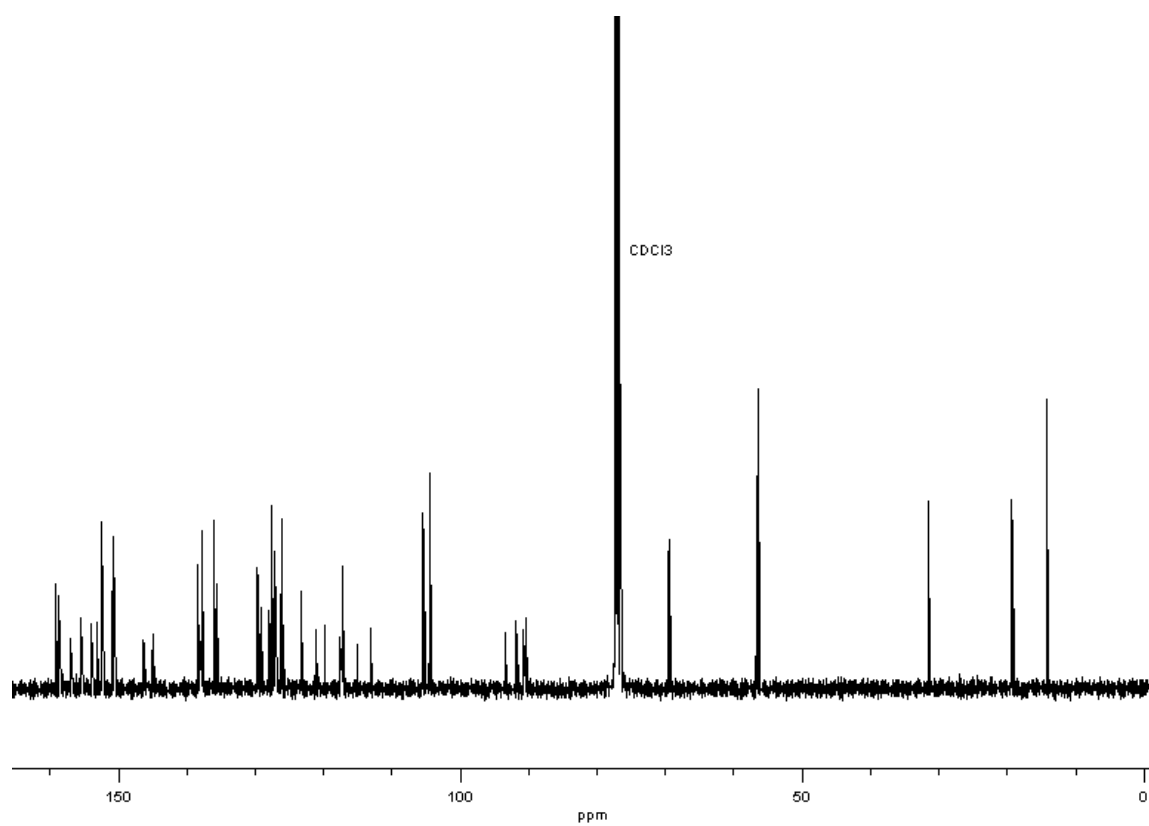


Figure S4. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **6**.

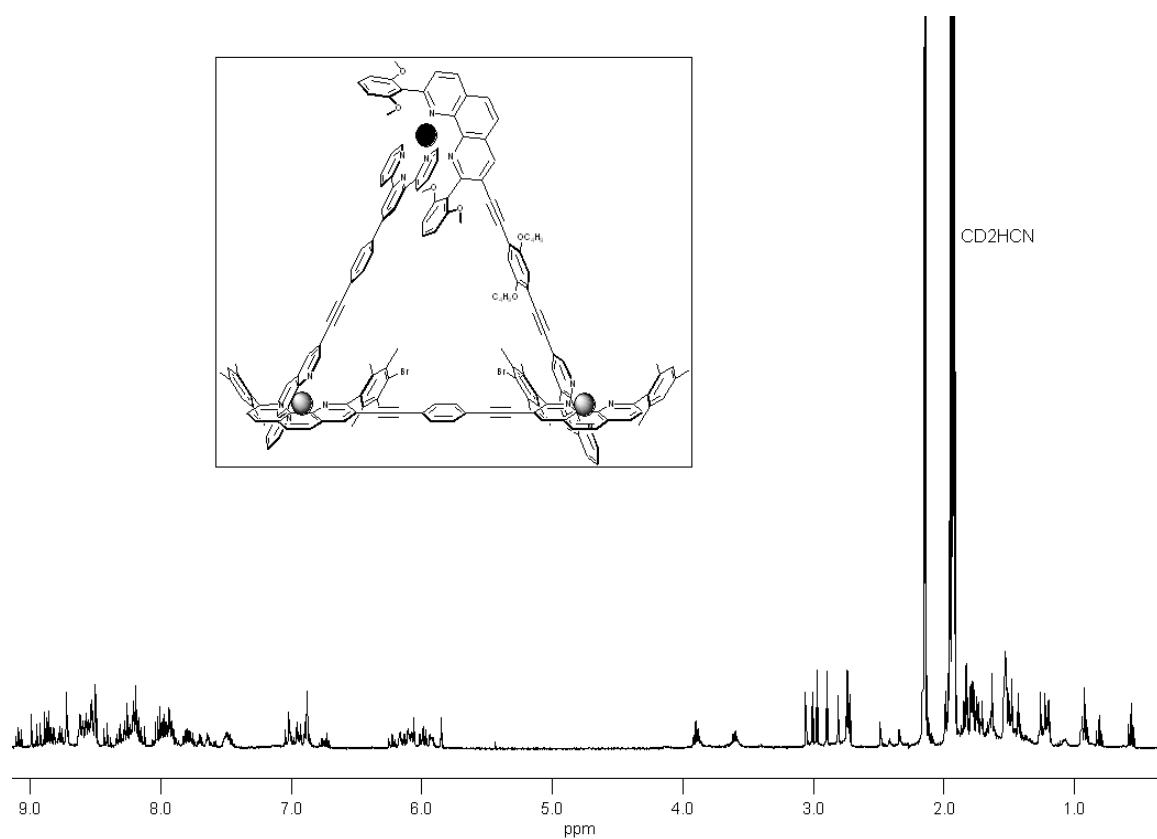


Figure S5. ^1H NMR spectrum (400 MHz, CD_3CN , 298 K) of **T** = $[\text{Cu}_2\text{Zn}(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{OTf})_2(\text{PF}_6)_2$.

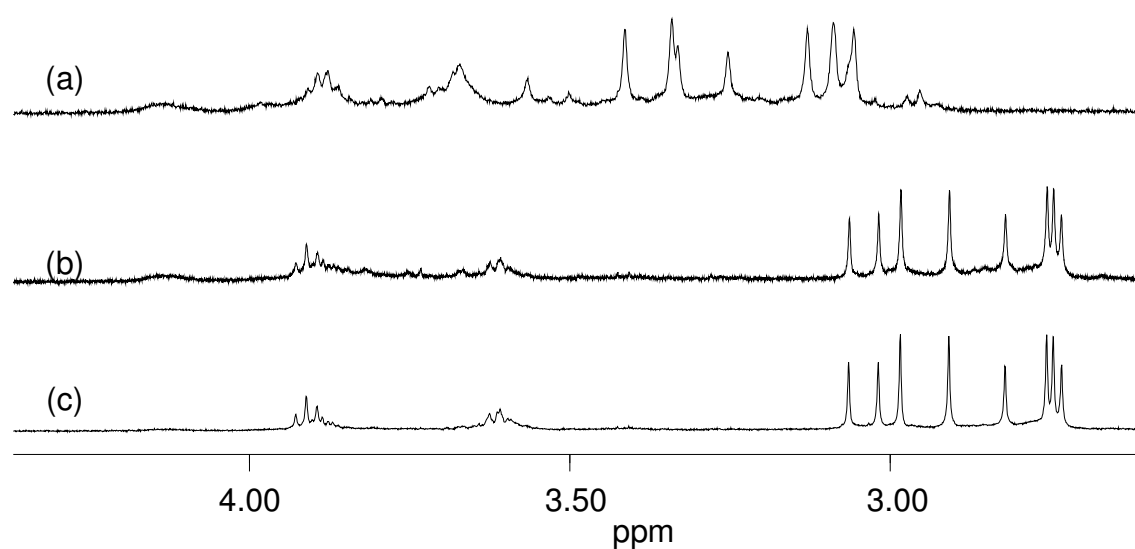


Figure S6. ^1H NMR spectra (400 MHz, CD_3CN , 298 K) of (a) $[\text{Cu}_3(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{PF}_6)_3$, (b) $[\text{Cu}_3(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{PF}_6)_3$ + one equiv. of Zn^{2+} and (c) **T** = $[\text{Cu}_2\text{Zn}(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{OTf})_2(\text{PF}_6)_2$.

ESI-MS spectra

km03-144_b#16-20 RT: 0,63-0,79 AV: 5 NL: 5,69E5

T: + c Full ms [150,00-2000,00]

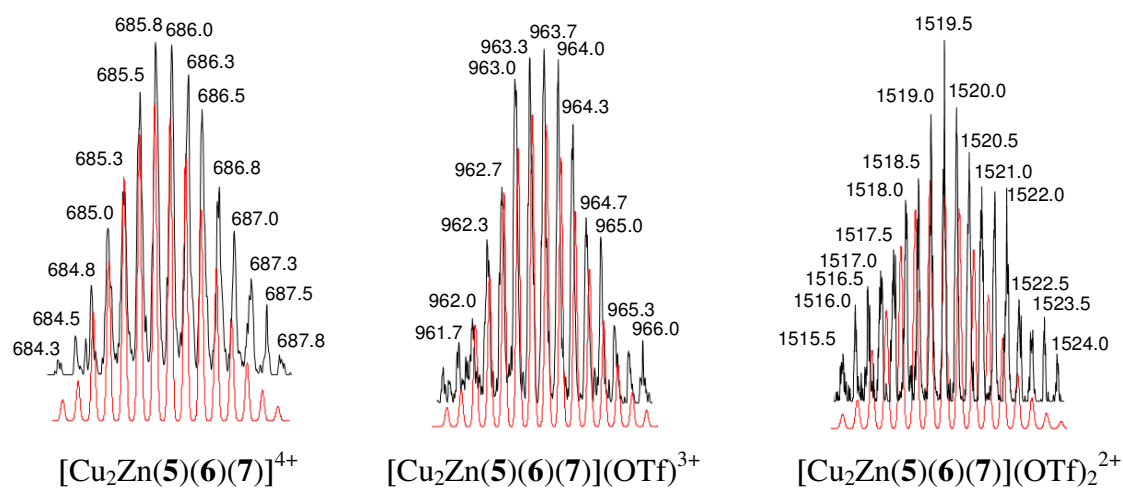
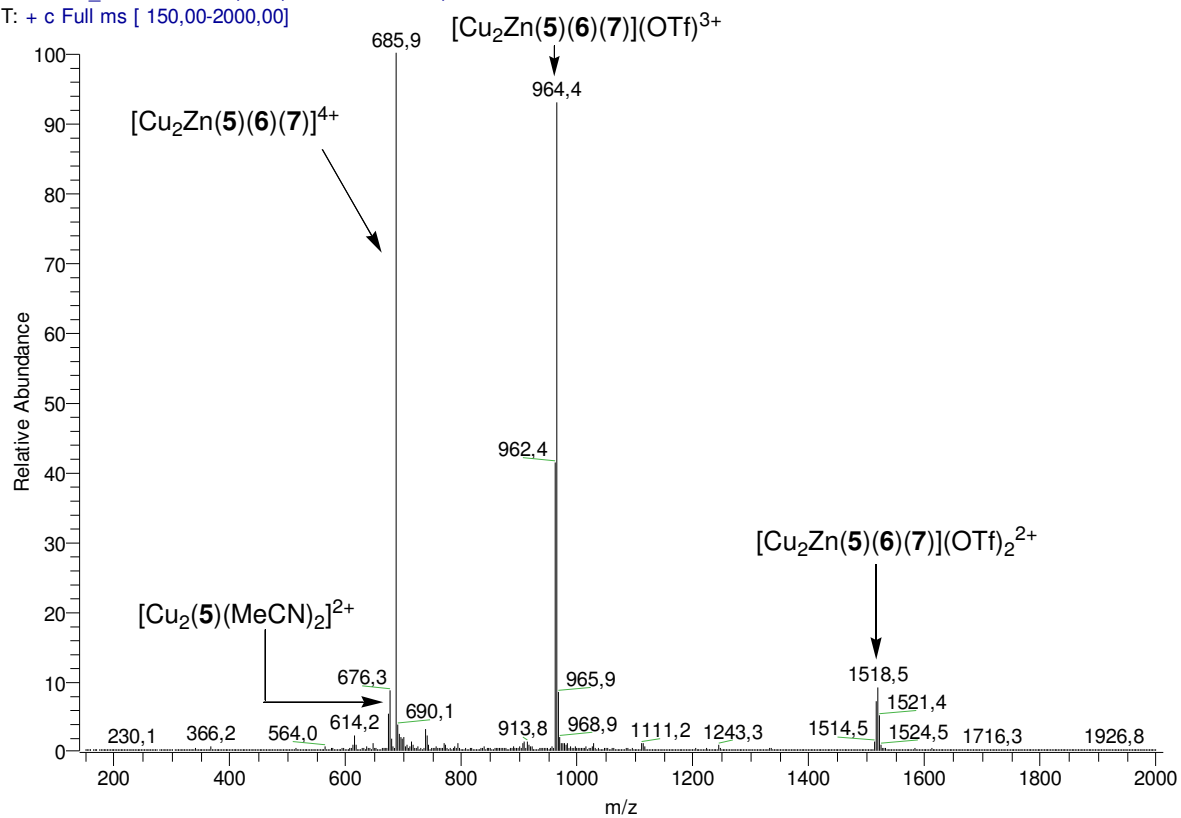


Figure S7. ESI-MS spectrum of **T** = $[\text{Cu}_2\text{Zn}(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{OTf})_2(\text{PF}_6)_2$ (in acetonitrile) and experimental isotopic distributions (black lines) along with calculated isotopic distributions (red lines) for the different charged species obtained after the loss of counter anion(s).

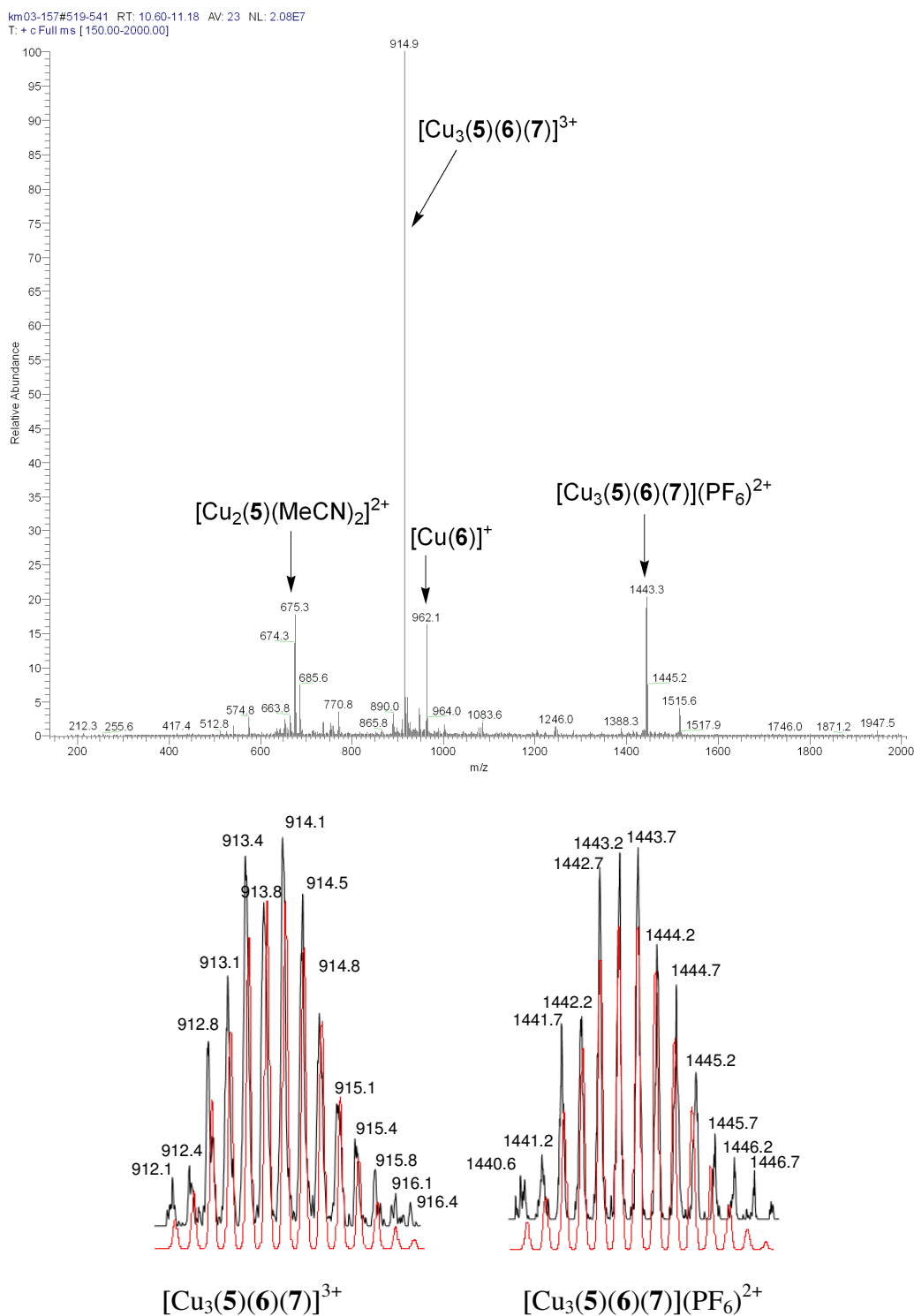


Figure S8. ESI-MS spectrum of homometallic triangle = $[Cu_3(5)(6)(7)](PF_6)_3$ (in acetonitrile) and experimental isotopic distributions (black lines) along with calculated isotopic distributions (red lines) for the different charged species obtained after the loss of counter anion(s).

km03-151#977-1002 RT: 21.57-22.43 AV: 26 NL: 1.27E6
T: + c Full ms [150.00-2000.00]

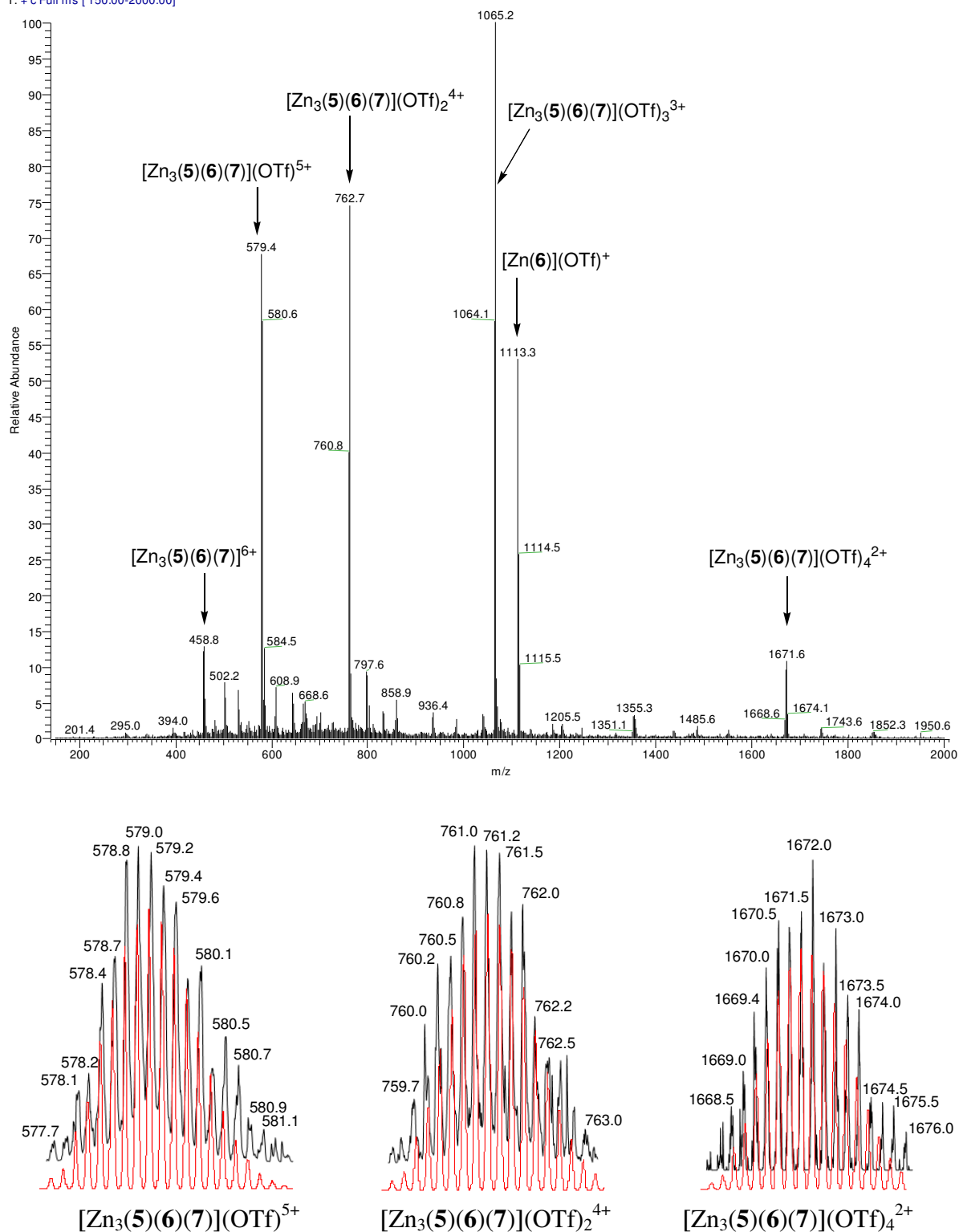


Figure S9. ESI-MS spectrum of homometallic triangle = $[\text{Zn}_3(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{OTf})_6$ (in acetonitrile) and experimental isotopic distributions (black lines) along with calculated isotopic distributions (red lines) for the different charged species obtained after the loss of counter anion(s).

DOSY

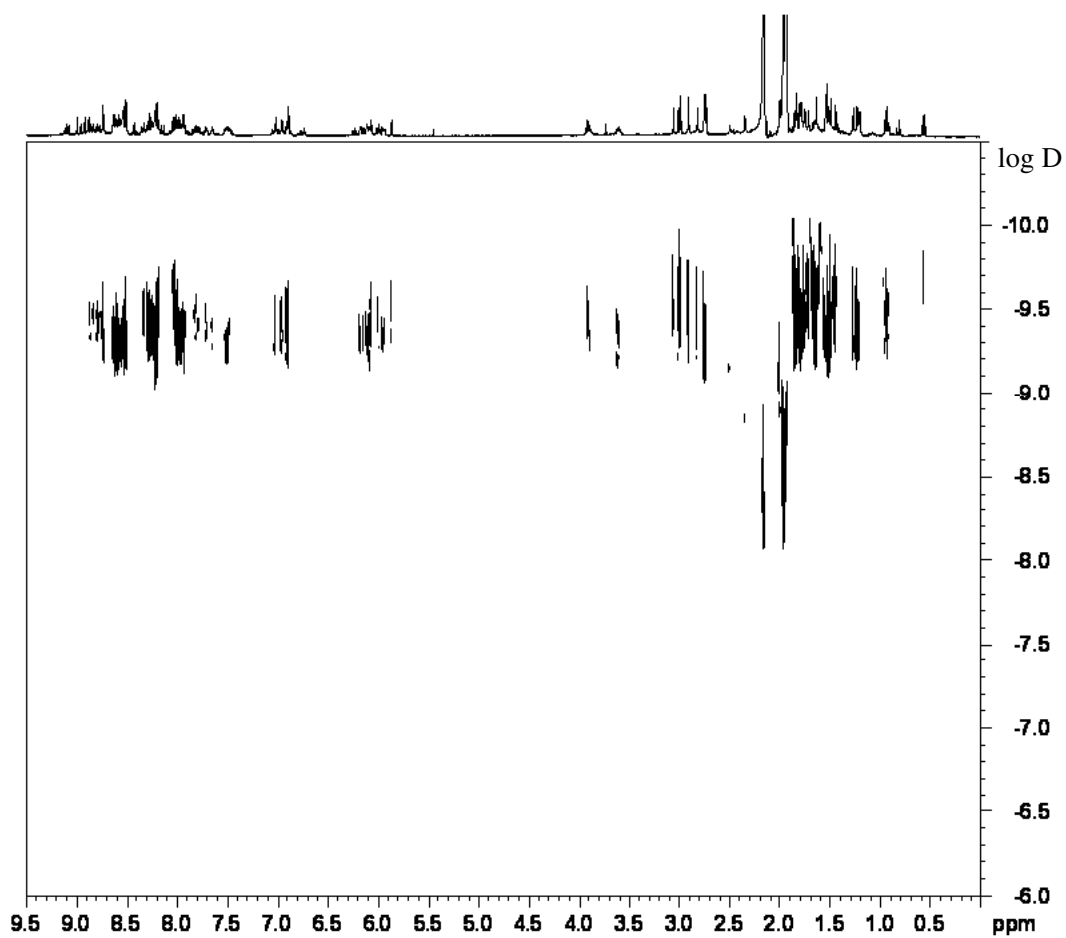


Figure S10. DOSY NMR of triangle **T** = [Cu₂Zn(**5**)(**6**)(**7**)](OTf)₂(PF₆)₂.

Differential pulse voltammetry (DPV)

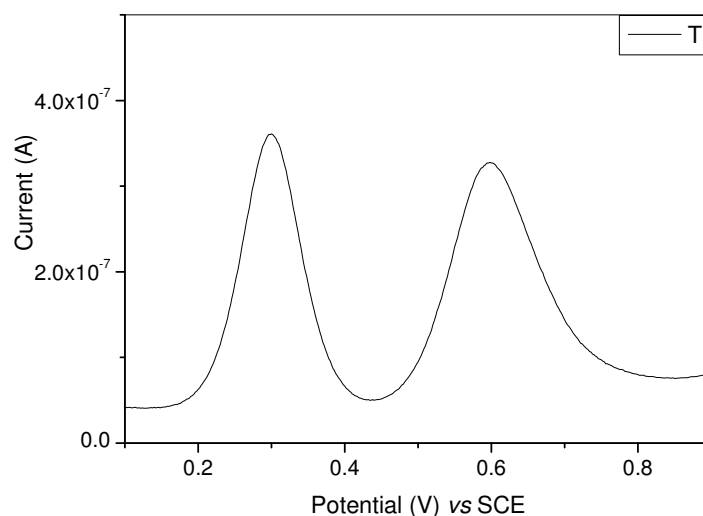


Figure S11. Differential pulse voltammetry (DPV) investigation of isosceles triangle **T** = $[\text{Cu}_2\text{Zn}(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{OTf})_2(\text{PF}_6)_2$. The experiment was carried out in dry acetonitrile with 0.1 M $n\text{Bu}_4\text{NPF}_6$ as electrolyte against a Ag wire as a quasi-reference electrode and 1,1'-dimethylferrocene (left wave) as internal standard (scan rate of 20 mVs^{-1} and a pulse height of 2 mV).

Deconvolution of the DPV

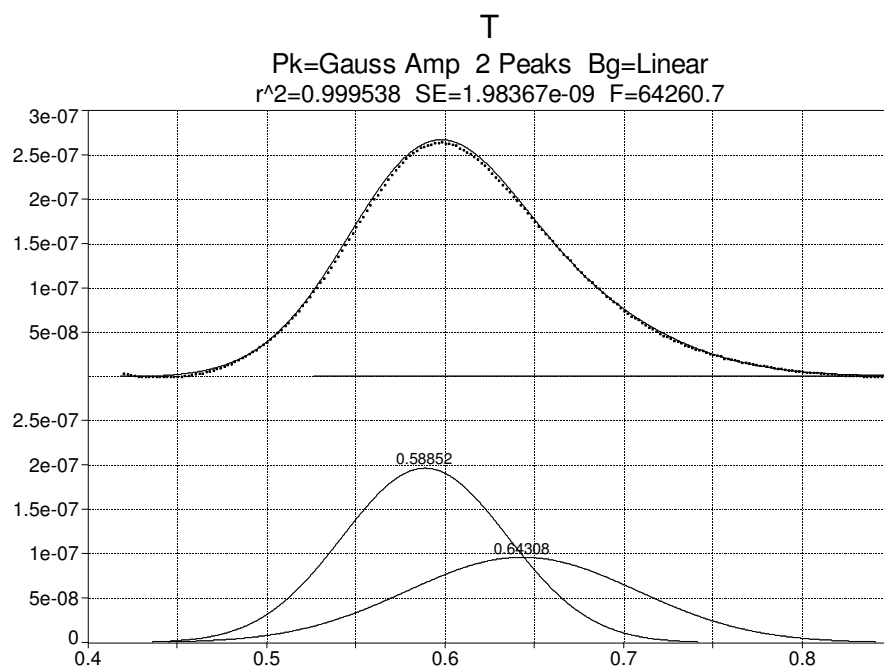


Figure S12. Deconvoluted differential pulse voltammogram of isosceles triangle **T** = $[\text{Cu}_2\text{Zn}(\mathbf{5})(\mathbf{6})(\mathbf{7})](\text{OTf})_2(\text{PF}_6)_2$.

Fitted Parameters

r ² Coef Det		DF Adj r ²	Fit Std Err	F-value
0.99953781		0.99951995	1.9837e-09	64260.7482
Peak	Type	a0	a1	a2
1	Gauss Amp	1.965e-07	0.58852392	0.04636793
2	Gauss Amp	9.6295e-08	0.64308477	0.06448259
B	Linear Bg	-3.051e-09	4.1249e-09	

Measured Values

Peak	Type	Amplitude	Center	FWHM	Asym50	FW Base
Asym10						
1	Gauss Amp	1.965e-07	0.58852392	0.10918813	1.00000004	0.21856278
	0.99999999					
2	Gauss Amp	9.6295e-08	0.64308477	0.15184490	1.00000000	0.30394919
	1.00000000					

Peak	Type	Anlytc Area	% Area	Int Area	% Area	Centroid
Moment2						
1	Gauss Amp	2.2839e-08	59.4713407	2.2836e-08	59.4905724	0.58854896
	0.00214576					
2	Gauss Amp	1.5565e-08	40.5286593	1.555e-08	40.5094276	0.64300002
	0.00411259					
	Total	3.8404e-08	100.000000	3.8386e-08	100.000000	

Parameter Statistics

Peak 1	Gauss Amp				
Parm	Value	Std Error	t-value	95	
Amp	1.965e-07	2.5313e-08	7.76302183	1.466e-07	2.4641e-07
Ctr	0.58852392	0.00064779	908.503622	0.58724683	0.58980100
Wid	0.04636793	0.00122236	37.9331514	0.04395813	0.04877773

Peak 2	Gauss Amp				
Parm	Value	Std Error	t-value	95	
Amp	9.6295e-08	1.7739e-08	5.42834121	6.1323e-08	1.3127e-07
Ctr	0.64308477	0.01237702	51.9579679	0.61868429	0.66748525
Wid	0.06448259	0.00361365	17.8441777	0.05735852	0.07160667

Baseline	Linear Bg				
Parm	Value	Std Error	t-value	95	
a0	-3.051e-09	1.5521e-09	-1.9655330	-6.11e-09	9.1598e-12
a1	4.1249e-09	1.9641e-09	2.10015976	2.5283e-10	7.9969e-09

Analysis of Variance

r ² Coef Det		DF Adj r ²	Fit Std Err	
0.99953781		0.99951995	1.9837e-09	
Source	Sum of Squares	DF	Mean Square	F
Regr	1.7700307e-12	7	2.5286152e-13	64260.748
Error	8.1846537e-16	208	3.9349297e-18	
Total	1.7708491e-12	215		

Details of Fit

Set Convergence	State	Iterations	Minimization	Extent
1E-6	Converged	45	Least Squares	1/1
Curvature Matrix	Constraints			Violated
Sparse-Roots	25.0000-5.00000-50.0000-	None	- None	0

References

- 1 M. Schmittl, C. Michel, A. Wiegrefe and V. Kalsani, *Synthesis*, 2001, 1561.
- 2 K. Mahata and M. Schmittl, *J. Am. Chem. Soc.*, 2009, **131**, 16544.