Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

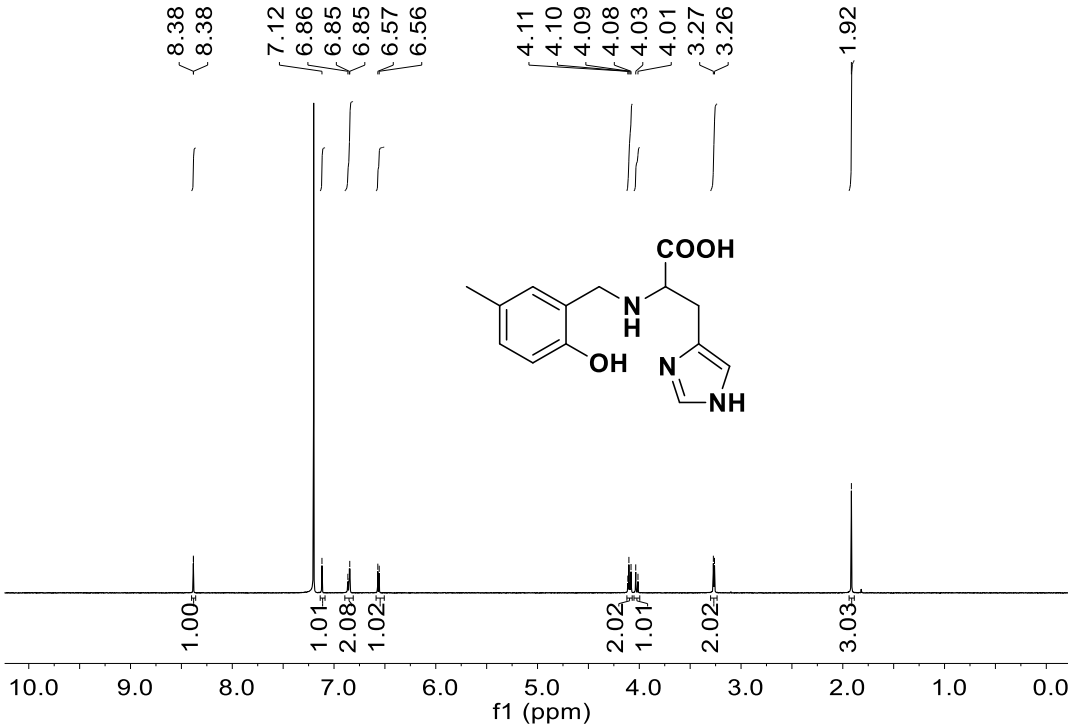

Figure S1. ^{1}H NMR spectrum of ligand HL^{1} (600 MHz, deuterium oxide -20% HCl).

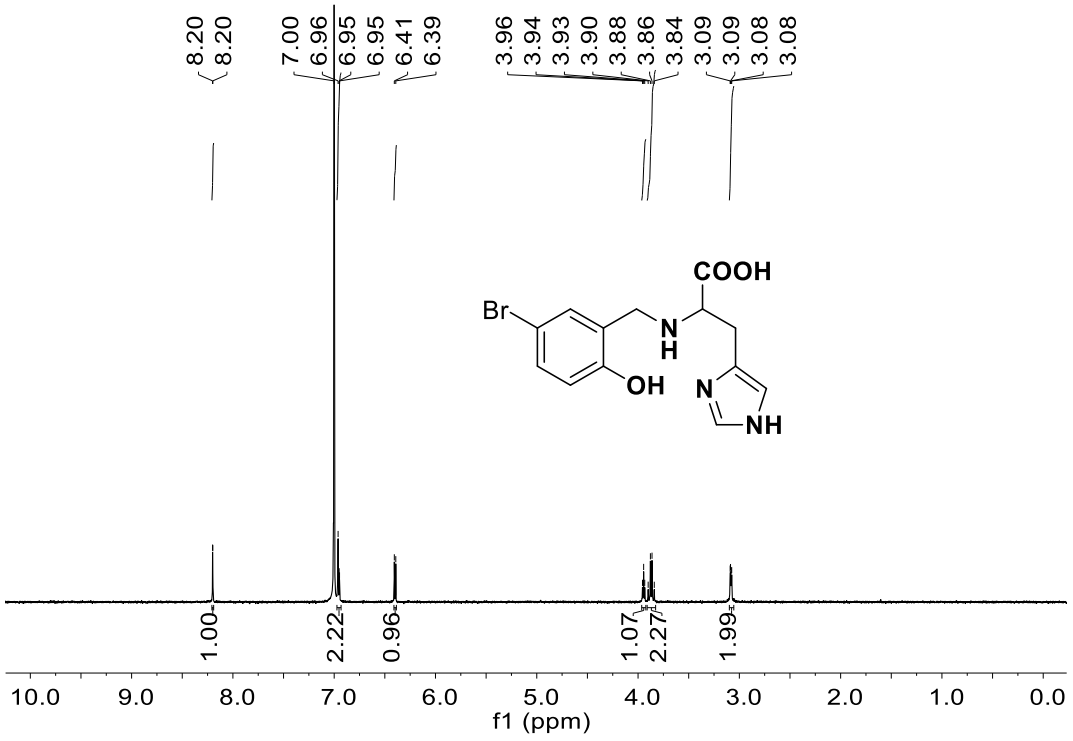

Figure S2. ^{1}H NMR spectrum of ligand HL^{2} (600 MHz, deuterium oxide-20% HCl).

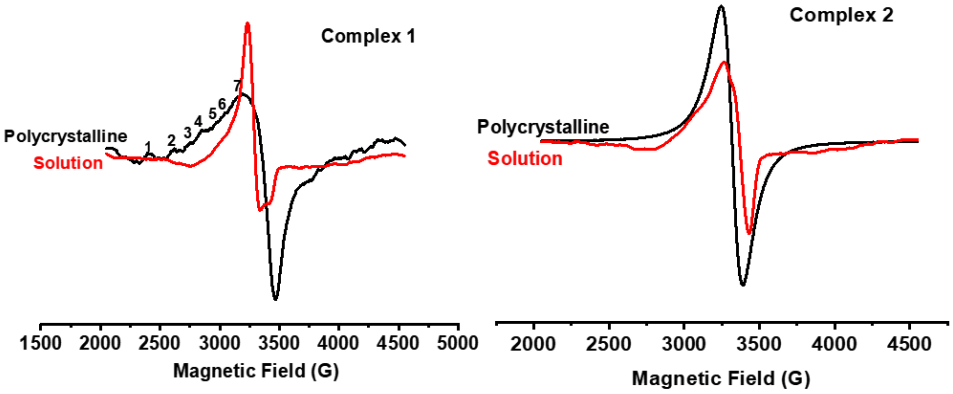

Figure S3 The EPR spectrum of complexes **1** and **2** at room temperature.

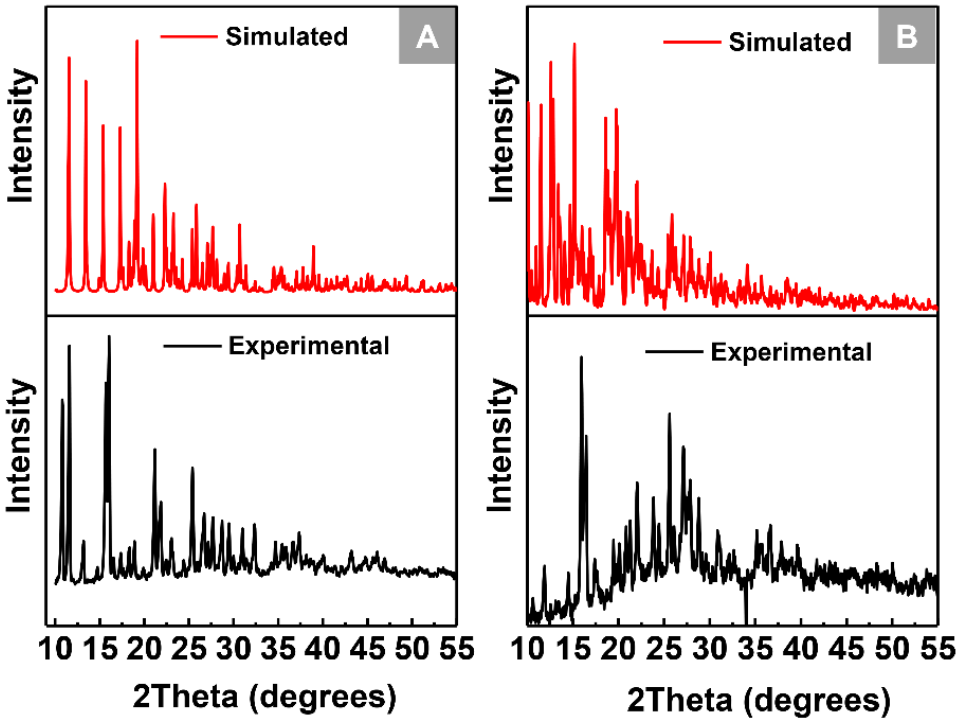

Figure S4. The measured and simulated XRD by Mercury for complexes **1** and **2**.

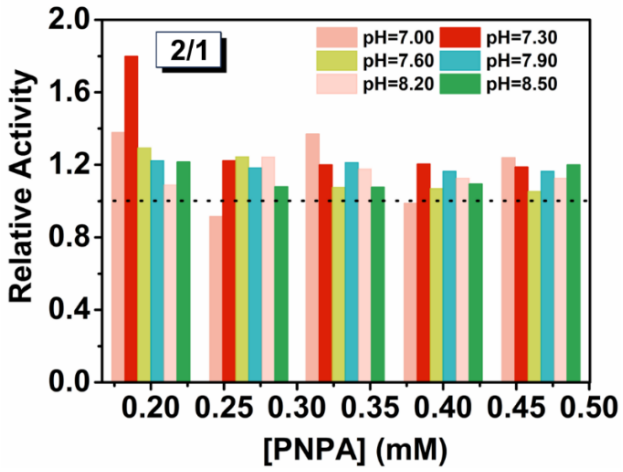

Figure S5. The relative activity between **2** and **1** for the PNPA catalytic hydrolysis.

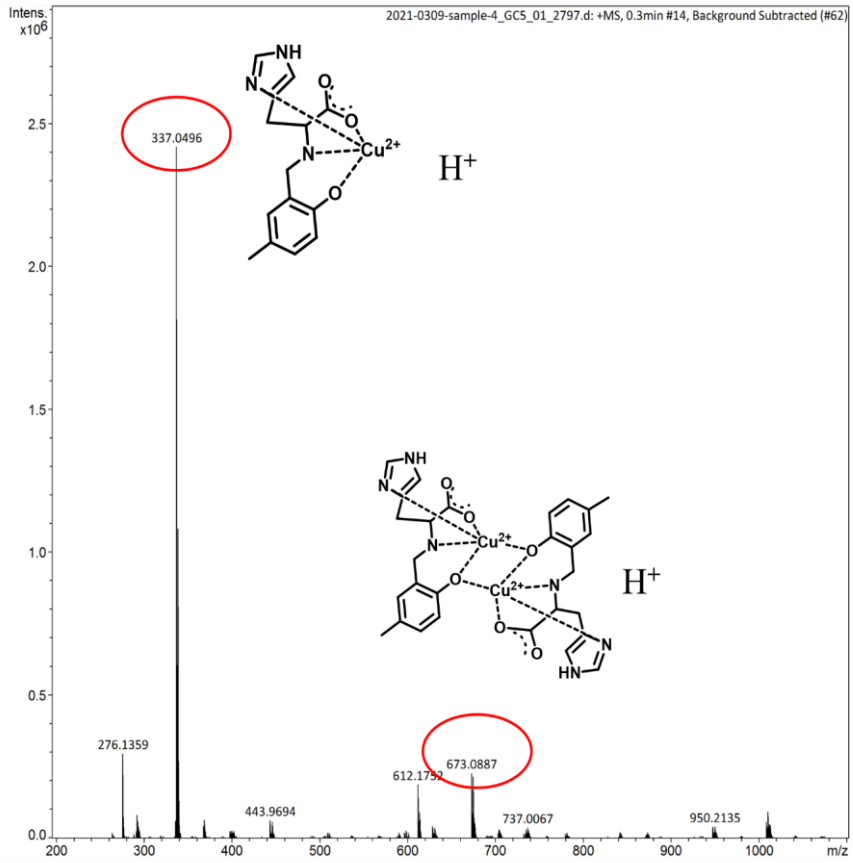

Figure S6. ESI^+-MS spectra for complex **1** in H_2O medium.

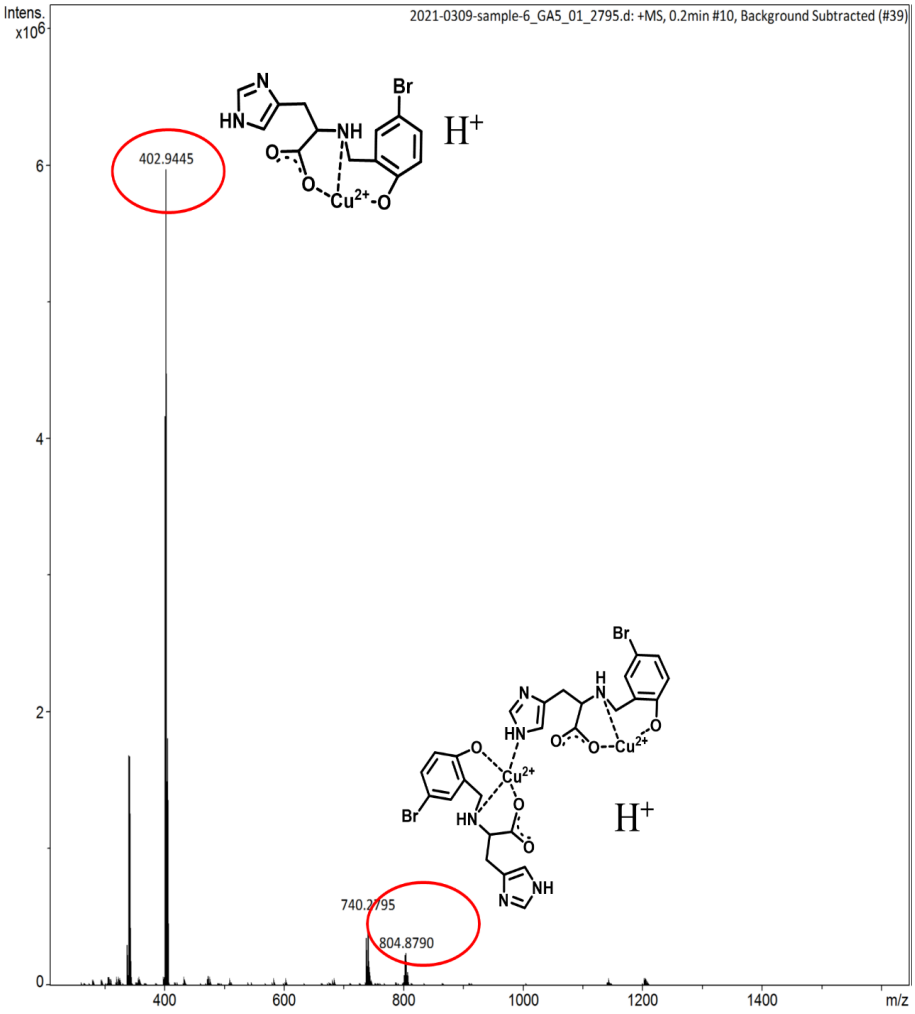

Figure S7. ESI$^+$-MS spectra for **2** in H_2O medium.

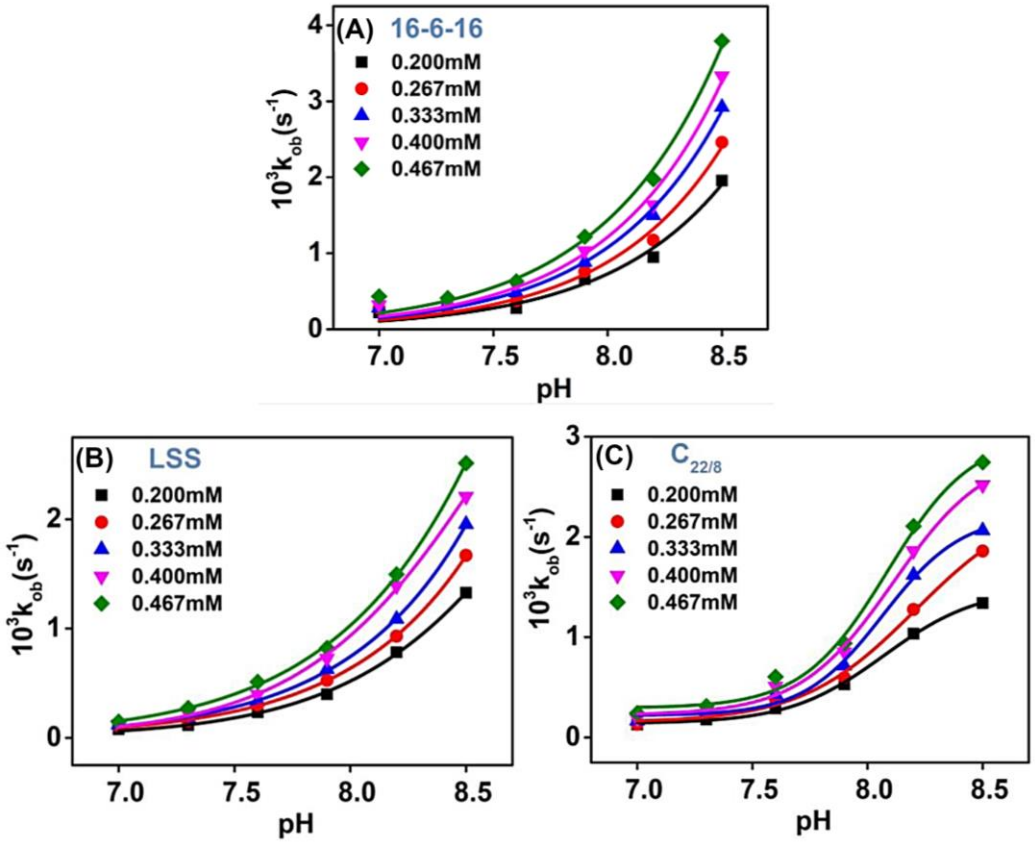

Figure S8. pH-Dependent hydrolysis of PNPA promoted by **1** in micellar solutions of 16-6-16 (A), LSS (B), and $C_{22/8}$ (C).

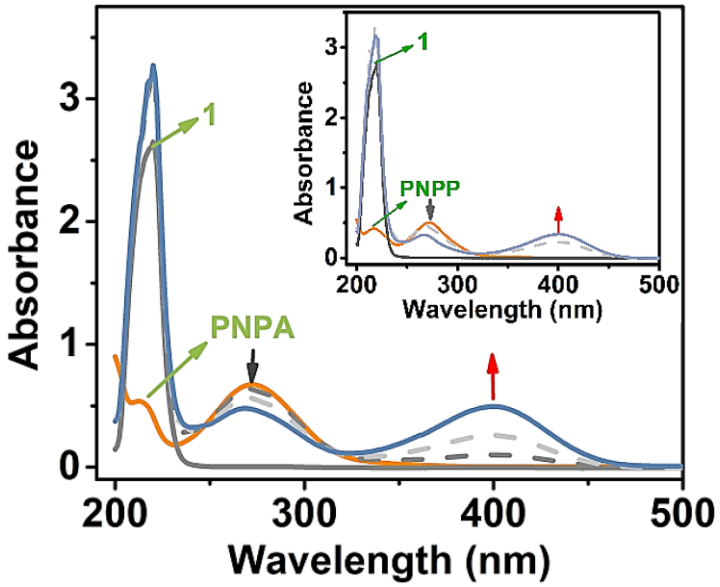

Figure S9. UV–Vis spectra for the hydrolysis of PNPA or PNPP (inset) by **1**.

Table S1. Selected bond length (Å) of **1** and **2**

Selected bond length (Å) of **1**	
Cu(1)-Cu(1^1)	3.0217(13)
Cu(1)-O(3)	1.942(4)
Cu(1)-O(3)	1.964(4)
Cu(1)-N(2)	1.993(5)
Cu(1)-N(1)	1.976(5)
Cu(1)-O(1)	2.183(4)
O(3)- Cu(1^1)	1.942(4)

Selected bond length (Å) of **2**			
Cu(1)-O(1)	1.895(4)	Cu(4)-N(10)	1.995(5)
Cu(1)-O(2)	1.967(4)	Cu(5)-O(22)	1.889(6)
Cu(1)-N(1)	2.007(5)	Cu(5)-O(23)	1.960(5)
Cu(1)-N(12)	1.978(5)	Cu(5)-N(21)	1.961(6)
Cu(2)-O(4)	1.906(5)	Cu(5)-N(22)	1.997(6)
Cu(2)-O(5)	1.976(4)	Cu(6)-O(13)	1.906(5)
Cu(2)-O(26)	2.383(8)	Cu(6)-O(14)	1.955(5)
Cu(2)-N(3)	1.963(5)	Cu(6)-N(13)	1.985(6)
Cu(2)-N(4)	1.994(5)	Cu(6)-N(24)	1.949(6)
Cu(3)-O(7)	1.902(4)	Cu(7)-O(16)	1.913(5)
Cu(3)-O(8)	1.961(4)	Cu(7)-O(17)	1.913(5)
Cu(3)-N(6)	1.963(5)	Cu(7)-N(15)	1.964(6)
Cu(3)-N(7)	1.997(4)	Cu(7)-N(16)	1.988(5)
Cu(4)-O(10)	1.904(5)	Cu(8)-O(19)	1.891(5)
Cu(4)-O(11)	1.974(4)	Cu(8)-O(20)	1.952(5)
Cu(4)-O(25)	2.414(9)	Cu(8)-N(18)	1.958(5)
Cu(4)-N(9)	1.957(5)	Cu(8)-N(19)	1.992(5)

Table S2. Selected bond angle (°) of **1** and **2**

Selected bond angle (°) of **1**			
O(3[1])-Cu(1)-Cu(1[1])	39.59(10)	O(3[1])-Cu(1)-O(1)	98.88(18)
O(3)-Cu(1)-Cu(1[1])	39.07(10)	N(2)-Cu(1)-Cu(1[1])	122.21(14)
O(3[1])-Cu(1)-O(3)	77.93(16)	N(2)-Cu(1)-O(1)	94.34(17)
O(3)-Cu(1)-N(2)	136.8(2)	N(1)-Cu(1)-Cu(1[1])	131.45(13)
O(3[1])-Cu(1)-N(2)	102.1(2)	N(1)-Cu(1)-N(2)	91.0(2)
O(3)-Cu(1)-N(1)	92.38(16)	N(1)-Cu(1)-O(1)	80.14(19)
O(3[1])-Cu(1)-N(1)	166.9(2)	O(1)-Cu(1)-Cu(1[1])	125.40(11)
O(3)-Cu(1)-O(1)	128.7(2)		
Selected bond angle (°) of **2**			
O(1)-Cu(1)-O(2)	173.0(3)	N(9)-Cu(4)-O(11)	91.3(2)
O(1)-Cu(1)-N(1)	94.05(18)	N(9)-Cu(4)-O(25)	97.0(3)
O(1)-Cu(1)-N(12)	90.05(18)	N(9)-Cu(4)-N(10)	171.9(2)
O(2)-Cu(1)-N(1)	84.02(17)	N(10)-Cu(4)-O(25)	89.1(3)
O(2)-Cu(1)-N(1)	91.96(18)	O(22)-Cu(5)-O(23)	172.2(4)
N(12)-Cu(1)-N(1)	175.87(19)	O(22)-Cu(5)-N(21)	89.7(2)
O(4)-Cu(2)-O(5)	173.4(2)	O(22)-Cu(5)-N(22)	94.1(2)
O(4)-Cu(2)-O(26)	97.6(3)	O(23)-Cu(5)-N(21)	92.2(2)
O(4)-Cu(2)-N(3)	90.6(2)	O(23)-Cu(5)-N(22)	83.5(2)
O(4)-Cu(2)-N(4)	94.7(2)	N(21)-Cu(5)-N(22)	174.7(2)
O(5)-Cu(2)-O(26)	88.4(3)	O(13)-Cu(6)-O(14)	166.3(4)
O(5)-Cu(2)-N(4)	82.46(18)	O(13)-Cu(6)-N(13)	94.2(2)
N(3)-Cu(2)-O(5)	91.5(2)	O(13)-Cu(6)-N(24)	90.6(2)
N(3)-Cu(2)-O(26)	97.7(3)	O(14)-Cu(6)-N(13)	83.4(2)
N(3)-Cu(2)-N(4)	171.0(2)	N(24)-Cu(6)-O(14)	94.1(2)
N(4)-Cu(2)-O(26)	88.9(3)	N(24)-Cu(6)-N(13)	169.3(3)
O(7)-Cu(3)-O(8)	178.38(19)	O(16)-Cu(7)-O(17)	173.1(3)
O(7)-Cu(3)-N(6)	89.72(18)	O(16)-Cu(7)-N(15)	90.7(2)
O(7)-Cu(3)-N(7)	94.71(17)	O(16)-Cu(7)-N(16)	94.1(2)
O(8)-Cu(3)-N(6)	91.61(18)	O(17)-Cu(7)-N(16)	83.0(2)
O(8)-Cu(3)-N(7)	83.94(17)	N(15)-Cu(7)-O(17)	91.7(2)
N(6)-Cu(3)-N(7)	175.50(19)	N(15)-Cu(7)-N(16)	173.4(2)
O(10)-Cu(4)-O(11)	173.8(2)	O(19)-Cu(8)-O(20)	169.0(3)
O(10)-Cu(4)-O(25)	97.8(3)	O(19)-Cu(8)-N(18)	89.7(2)
O(10)-Cu(4)-N(9)	90.6(2)	O(19)-Cu(8)-N(19)	94.63(19)
O(10)-Cu(4)-N(10)	93.9(2)	O(20)-Cu(8)-N(18)	92.30(19)
O(11)-Cu(4)-O(25)	87.8(3)	O(20)-Cu(8)-N(19)	83.86(19)
O(11)-Cu(4)-N(10)	83.45(19)	N(18)-Cu(8)-N(19)	175.0(2)

Table S3. Calculated Addison Tau factors (τ) and geometry for central copper(II) ions of **1** and **2**

Catalyst	Calculated Addison Tau factors (τ) and geometry			
1	Cu(1)		Cu(2)	
	τ	geometrical shape	τ	geometrical shape
	0.86	distorted trigonal bipyramid	0.71	distorted trigonal bipyramid
2	Cu(1)		Cu(2)	
	τ	geometrical shape	τ	geometrical shape
	0.08	square pyramid	0.11	distorted square pyramid
	Cu(3)		Cu(4)	
	τ	geometrical shape	τ	geometrical shape
	0.04	square pyramid	0.10	distorted square pyramid
	Cu(5)		Cu(6)	
	τ	geometrical shape	τ	geometrical shape
	0.09	distorted square pyramid	0.17	distorted square pyramid
	Cu(7)		Cu(8)	
	τ	geometrical shape	τ	geometrical shape
	0.10	distorted square pyramid	0.11	distorted square pyramid

Table S4. Pseudo first-order rate constants of PNPP hydrolysis catalyzed by **1** or **2** in buffered aqueous solution

Complex	pH	10^3[S](mol/L)				
		0.200	0.267	0.333	0.400	0.467
		$10^3 k_{ob}(s^{-1})$				
1	7.00	5.57	6.09	7.70	8.63	9.08
	7.30	5.87	7.82	8.72	9.83	11.2
	7.60	6.57	8.32	9.35	11.3	12.2
	7.90	7.81	10.3	11.8	13.7	14.7
	8.20	8.87	12.4	14.3	16.7	18.7
	8.50	11.7	15.1	20.0	21.9	27.4
2	7.00	13.2	16.2	17.6	19.3	20.9
	7.30	14.4	17.0	20.1	19.6	23.3
	7.60	13.7	17.7	18.9	21.5	23.9
	7.90	14.2	17.5	20.7	23.2	26.2
	8.20	15.5	20.5	23.2	27.8	29.1
	8.50	19.9	24.6	28.0	32.7	35.4

Conditions: 25 ℃, I= 0.1 M KCl, [complex]= 1.0×10^{-5} mol/L.

Table S5. Apparent first-order rate constants of PNPA mediated by **2** in various micelles

		$10^3 k_{ob}(s^{-1})$				
Micelle	pH	[S] 0.200 mM	0.267	0.333	0.400	0.267
16-6-16	7.00	0.258	0.290	0.351	0.360	0.420
	7.30	0.222	0.278	0.350	0.430	0.474
	7.60	0.347	0.427	0.537	0.604	0.692
	7.90	0.646	0.896	1.03	1.18	1.37
	8.20	1.05	1.36	1.70	2.01	2.19
	8.50	2.28	3.19	3.44	4.14	4.55
$C_{22/8}$	7.00	0.129	0.172	0.178	0.190	0.199
	7.30	0.188	0.229	0.252	0.326	0.338
	7.60	0.266	0.315	0.459	0.490	0.578
	7.90	0.557	0.600	0.791	0.831	0.984
	8.20	0.975	1.29	1.50	1.82	2.19
	8.50	1.19	1.64	2.07	2.30	2.83
LSS	7.00	0.0856	0.0972	0.115	0.141	0.155
	7.30	0.0902	0.166	0.201	0.214	0.275
	7.60	0.216	0.306	0.346	0.400	0.475
	7.90	0.466	0.544	0.650	0.789	0.889
	8.20	0.707	0.873	1.06	1.23	1.51
	8.50	1.18	1.47	1.93	2.10	2.35

Conditions: 25 °C, I= 0.1 M KCl, [**2**]= 1.0×10^{-5} mol/L, [16–6-16]=1.0×10^{-4} mol/L, [$C_{22/8}$]= 1.0×10^{-4} mol/L, [LSS]= 5.0×10^{-3} mol/L.

Table S6. Apparent first-order rate constants of PNPA mediated by **1** in various micelles

		$10^3 k_{ob}(s^{-1})$				
Micelle	**pH**	**[S] 0.200 mM**	**0.267**	**0.333**	**0.400**	**0.267**
16-6-16	7.00	0.222	0.276	0.281	0.319	0.432
	7.30	0.275	0.309	0.341	0.353	0.410
	7.60	0.278	0.374	0.481	0.578	0.630
	7.90	0.656	0.762	0.880	1.03	1.22
	8.20	0.949	1.172	1.50	1.63	1.98
	8.50	1.95	2.46	2.92	3.33	3.79
$C_{22/8}$	7.00	0.127	0.131	0.167	0.188	0.243
	7.30	0.179	0.216	0.243	0.274	0.313
	7.60	0.288	0.383	0.431	0.509	0.604
	7.90	0.529	0.597	0.715	0.850	0.938
	8.20	1.04	1.23	1.62	1.86	2.11
	8.50	1.34	1.86	2.06	2.52	2.75
LSS	7.00	0.078	0.105	0.120	0.126	0.148
	7.30	0.116	0.151	0.181	0.221	0.272
	7.60	0.234	0.302	0.334	0.397	0.511
	7.90	0.399	0.525	0.626	0.727	0.821
	8.20	0.784	0.929	1.09	1.39	1.50
	8.50	1.33	1.67	1.95	2.21	2.51

Conditions: 25 °C, I= 0.1 M KCl, [**1**]= 1.0×10^{-5} mol/L, [16–6-16]=1.0×10^{-4} mol/L, [$C_{22/8}$]= 1.0×10^{-4} mol/L, [LSS]= 5.0×10^{-3} mol/L.