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Supporting Information

Synthesis, Structure and Catalytic Application of Amidoterephthalate Copper Complexes in Diastereoselective Henry Reaction in Aqueous Medium

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Table S1: Crystal data and structure refinement details for H_2L1, H_2L2, complex 1 and complex 2

Identification name	**H_2L1**	**H_2L2**	**Complex 1**	**Complex 2**
Formulae	$C_{17}H_{25}N_3O_7$	$C_{11}H_{13}NO_6$	$C_{11}H_{17}CuNO_9$	$C_{10}H_{15}CuNO_9$
Mol. wt.	383.40	255.22	370.79	356.77
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P2(1)/c	P-1	P-1
Temperature /K	296	296	150	296
Wavelength /Å	0.71073	0.71073	0.71073	0.71073
a /Å	7.8968(15)	8.2402(4)	7.4875(3)	7.5580(10)
b /Å	8.8683(18)	15.2755(8)	9.4303(3)	9.2626(13)
c /Å	16.015(3)	9.6698(5)	10.4406(4)	10.5360(14)
α/°	99.775(7)	90.00	78.225(2)	104.104(4)
β/°	98.719(7)	*98.276(2)*	84.542(2)	90.218(4)
γ/°	111.790(7)	90.00	83.261(2)	96.517(5)
V/ Å^3	997.7(3)	1204.49(11)	714.78(5)	710.35(17)
Z	2	4	2	2
Density/Mgm^{-3}	1.276	1.407	1.723	1.668
Abs. Coeff. /mm^{-1}	0.100	0.116	1.575	1.581
F(000)	408	536	382	366
Refl. collected	14662	21464	5462	17154
Refl. unique	3652	2214	2594	2607
Max. 2θ/°	25.35	25.37	25.38	25.53
Ranges (h, k, l)	-9<= h <=9 -10 <= k <=10 -19 <= l <= 19	-9<= h <=9 -18 <= k <=18 -11 <= l <= 11	-7<= h <=9 -11 <= k <=11 -12 <= l <= 12	-9 <= h <=9 -11 <= k <=11 -12 <= l <= 12
Complete to 2θ (%)	99.9	100	98.3	97.9
Refl. with I > 2σ(I)	1863	1542	2181	2451
Data/ Restraints/Parameters	3652/0/250	2214/0/ 168	2594/ 8 / 224	2607 /8 / 213

Goof (F^2)	1.011	1.017	1.059	1.126
R1 [I > 2s(I)]	0.0832	0.0497	0.0439	0.0386
wR2 [I > 2s(I)]	0.2266	0.1254	0.1047	0.1043
R1 [all data]	0.1473	0.0778	0.0553	0.0415
wR2 [all data]	0.2831	0.1419	0.1114	0.1095

Table S2: Hydrogen bond geometry (Å, °) in compounds H_2L1, H_2L2, complex 1 and complex 2

Compound	D-H---A	D···H (Å)	H···A (Å)	D···A (Å)	<D–H···A(°)
H_2L1	N1-H1·····O4	0.86	1.98	2.680(4)	138
	O2-H2o·····O6	0.82	1.77	2.584(4)	173
	O3-H3o·····O7	0.82	1.75	2.560(3)	169
	C3-H3·····O7	0.93	2.60	3.366(5)	141
	C8-H8·····O5	0.93	2.19	2.824(5)	124
	C14-H14·····O1	0.93	2.54	3.215(5)	130
H_2L2	N1-H1·····O1	0.86	1.93	2.656(2)	141
	O2-H2o·····O6	0.82	1.74	2.554(3)	170
	O4-H4o·····O5	0.82	1.86	2.632(2)	157
	O6-H6·····O3	0.82	1.91	2.731(3)	175
	C10-H10A·····O3	0.96	2.61	3.501(3)	153.6
Complex 1	N1-H1·····O1	0.86	1.96	2.673(4)	139
	O12-H12A·····O5	0.931(19)	2.08(2)	2.982(4)	164(4)
	O12-H12B·····O2	0.945(19)	2.01(2)	2.953(4)	174(4)
	O13-H13A·····O3	0.865(19)	2.05(2)	2.918(4)	177(4)
	O13-H13B·····O4	0.867(19)	1.92(2)	2.773(4)	166(4)
	O14-H14A·····O4	0.955(19)	2.08(2)	3.021(5)	166(4)
	O14-H14B·····O3	0.936(19)	2.10(2)	3.027(4)	171(4)
	O15-H15A·····O13	0.948(19)	2.48(2)	3.406(5)	166(4)
	O15-H15B·····O3	0.947(19)	2.43(2)	3.363(5)	169(4)
Complex 2	N1-H1·····O1	0.86	1.91	2.634(3)	140
	O11-H11A·····O2	0.944(19)	2.04(2)	2.954(3)	163(3)
	O11-H11B·····O3	0.922(19)	2.01(2)	2.919(4)	169(3)
	O12-H12A·····O13	0.82	2.48	3.275(4)	163
	O13-H13B·····O4	0.883(19)	1.948(19)	2.829(3)	175(4)
	O13-H13A·····O3	0.884(19)	1.93(2)	2.800(3)	168(3)
	O14-H14A·····O4	0.909(19)	2.10(2)	2.989(3)	166(3)
	O14-H14B·····O3	0.957(19)	2.15(2)	3.047(4)	156(3)

Table S3: Selected bond distances (Å) and angles (°) for complex 1 and complex 2

Complex 1	Cu1-O1, 2.001(2); Cu1-O12, 1.996(3); Cu1-O13, 2.417(3); Cu1-O14, 2.007(3); Cu1-O15, 2.028(4); <O12-Cu1-O14, 165.46(14); <O12-Cu1-O1, 87.57(12); <O14-Cu1-O1, 91.89(12); <O12-

	Cu1-O15, 89.24(14); <O14-Cu1-O15, 91.45(15); <O1-Cu1-O15, 176.66(13); <O12-Cu1-O13, 104.05(12); <O14-Cu1-O13, 90.48(12); <O1- Cu1-O13, 93.65(10); <O15-Cu1-O13, 86.16(13)
Complex 2	Cu1-O1, 1.9903(19); Cu1-O11, 1.996(3); Cu1-O12, 2.027(3); Cu1-O13, 2.398(2); Cu1-O14, 2.011(3) <O1-Cu1-O11, 87.93(10); <O1-Cu1-O14, 90.25(10); <O11-Cu1-O14, 164.27(12); <O1-Cu1-O12, 176.48(9); <O11-Cu1-O12, 90.37(11); <O14-Cu1-O12, 92.21(12); <O1-Cu1-O13, 87.95(8); <O11-Cu1-O13, 104.06(10); <O14-Cu1-O13, 91.48(10); <O12-Cu1-O13, 89.48(10);

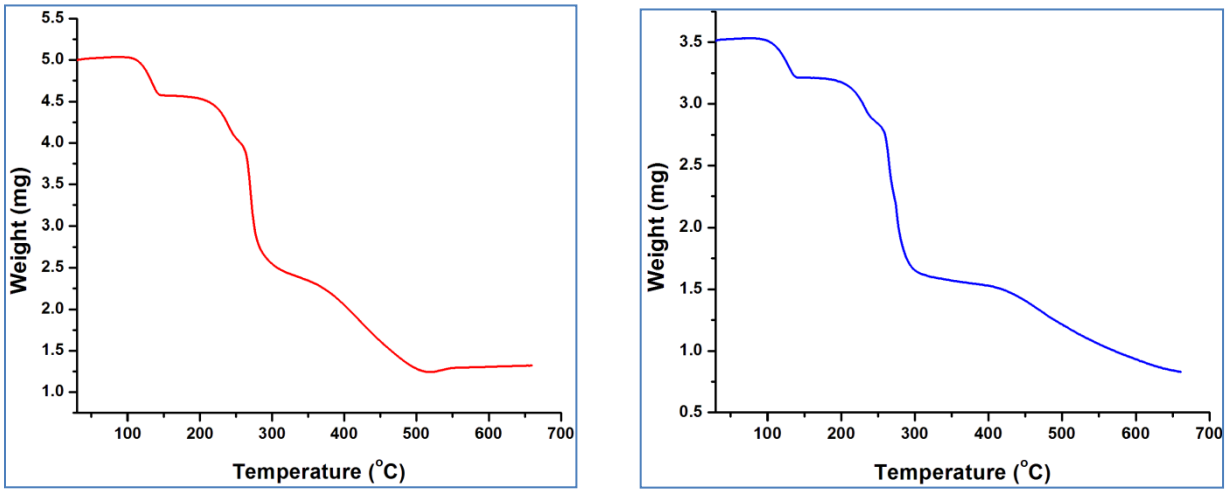

Figure S1: Thermogravimetric curves for complex **1** (A) and complex **2** (B).

Calculation of the yield and selectivity for compound 1 in the Henry reaction

Relative amounts of compounds (see Fig. S11):

Bezaldehyde + *anti* + *syn* = 1 + 0.6 + 2.75 = 4.35

Percentage of the unreacted bezaldehyde:

1/4.35 x 100= 23%

Conversion of benzaldehyde = yield of β-nitroalkanols = 100 – 23 = 77 %.

Yield of *anti*:

0.6/4.35x100= 13.8%

Yield of *syn*:

2.75/4.35x100= 63.2%

***Selectivity*:**

Sum of *anti* + *syn* = 13.8+ 63.2 = 77%

Selectivity of *anti*:

13.8/77x100= 18%

Selectivity of *syn*:
63.2/77x100= 82%

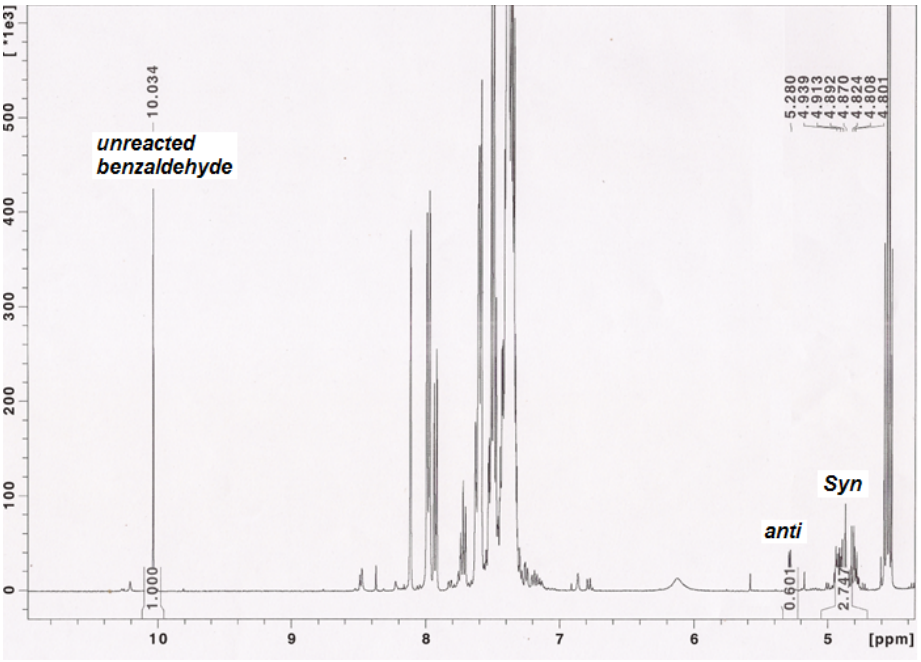

Figure S2**.** Example of integration in the ^{1}H-NMR spectrum for the determination of Henry reaction products (Table 1, Entry 5).

Crystal structure analysis of pro-ligands

The molecular structures of compounds H_2L1 and H_2L2 are shown in Figures S3A and S3B. In both structures the hanging amide and carboxylic groups are almost in the same plane with the phenyl ring. In H_2L1, not only the carboxylic groups are engaged in extensive strong COOH····O hydrogen bonding interactions with the surrounding DMF molecules ($d_{D–A}$ 2.560(3)Å; <D–H····A 169˚. $d_{D–A}$ 2.584(4)Å; <D–H····A 173˚), but also the amide oxygen atoms of the former participate in weak C-H····O contacts with the methyl hydrogen atoms of the latter thus forming a double chain 1D hydrogen-bonded network (Figure S4). Additionally, the amide NH- is intramolecularly hydrogen bonded with a carboxylate oxygen atom ($d_{D–A}$ 2.680(4)Å; <D–H····A 138˚).

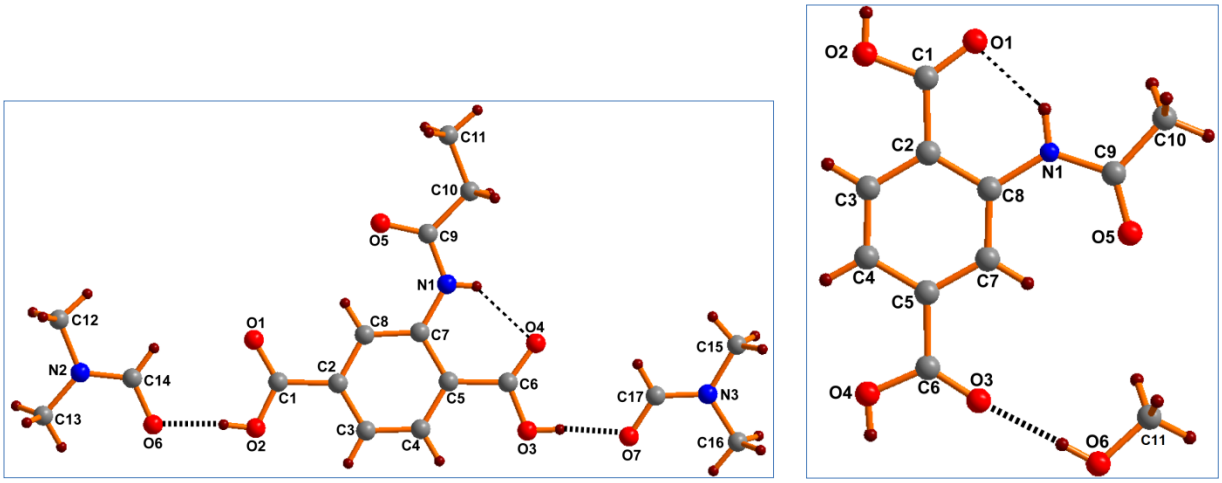

Figure S3: (A) Crystal structure of H_2L1, hydrogen bonded with DMF molecules. (B) Crystal structure of H_2L2, hydrogen bonded with methanol molecule.

In the case of H_2L2, the methanol molecules simultaneously act as H-acceptor ($d_{D–A,}$ 2.554(3)Å; <D–H····A 170˚) and H-donor ($d_{D–A,}$ 2.731(3)Å; <D–H····A 175˚) to carboxylic groups of vicinal H_2L2 molecules and together with the strong intermolecular NH–O interaction ($d_{D–A}$ 2.656(2)Å; <D–H····A 141˚) they form a $C_2^2(11)$ graph set. The intermolecular organization in this compound is directed by H_2L2–H_2L2 as well as H_2L2–methanol O–H····O hydrogen bonds (Figure S5) thus representing a continuous two dimensional supramolecular assembly of the component species.

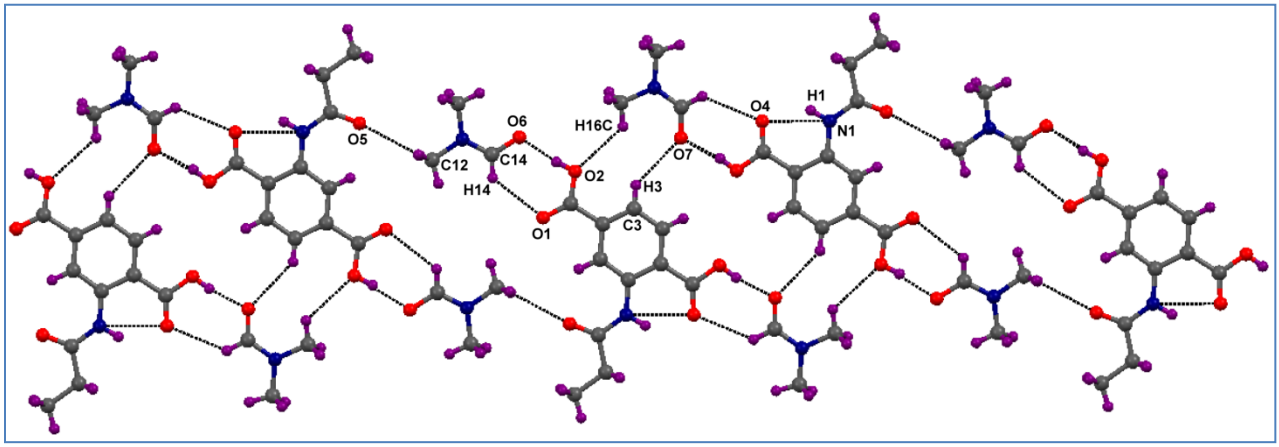

Figure S4: One dimensional hydrogen bonded network of H_2L1 and DMF molecules

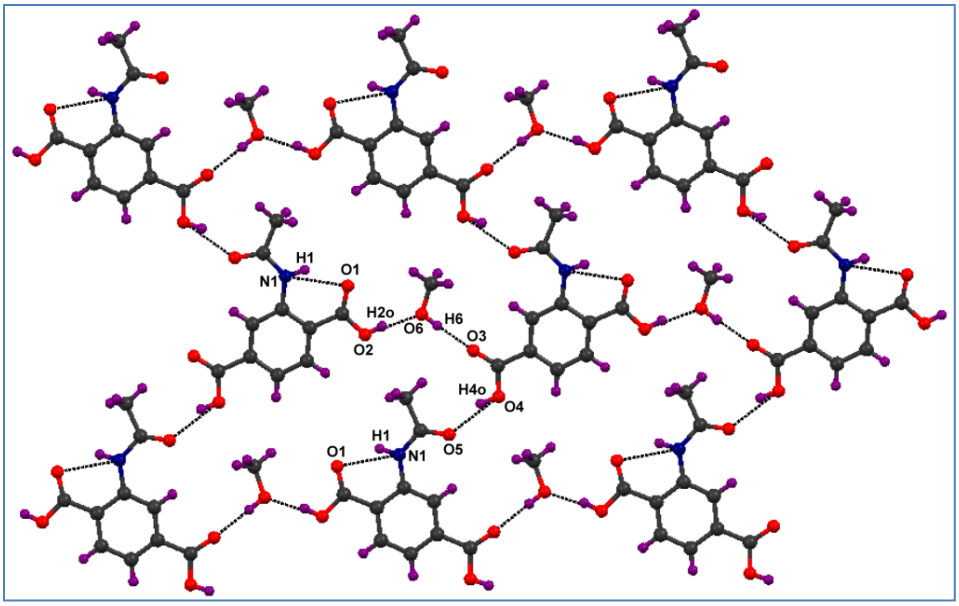

Figure S5: Two dimensional hydrogen bonded network of H_2L2 and methanol molecules