Electronic Supplementary Material (ESI) for Chemical Science

Exploring frontiers of high surface area metal-organic frameworks

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Supporting Information

Statistical model for mass of alchemical molecules

Figure S1 illustrates the statistical model utilized during optimization to predict the mass of alchemical ligands based upon their absolute surface area. The model is built on 240 commercially available dicarboxylate ligands with exclusively carbon and hydrogen backbones.

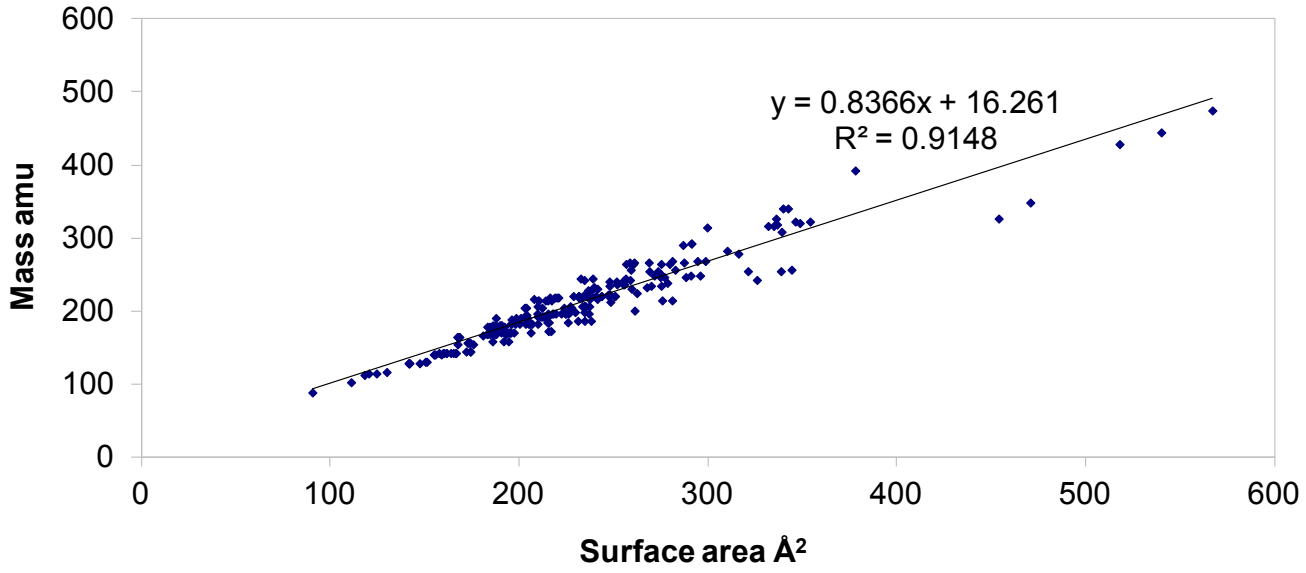

Figure S1. A statistical model correlates the surface area of ligands with their mass; this model was used to predict the mass of alchemical molecules in the optimization algorithm.

Geometrical parameters of alchemical ligands

Alchemical ligands comprise two fragments, the choice of which determines the connectivity of the ligand, and accordingly the MOF net which results (restricted to the six nets examined in this work). For a pair of fragments, the shape of each ligand is then governed by nine geometrical parameters pertaining to these fragments (r_1, r_2, l_2 and r_3 for each fragment) and the distance between them, l_1; hence, for each fragment combination, optimization takes place within a nine-dimensional space of possible ligands. This space is discretized to a 0.1Å resolution.

The space of possible ligands is bounded in each of the nine geometrical dimensions. The bounds were chosen to a) reflect the feasibility of particular molecular substructures; b) examine the effect on framework surface area of pushing the limits of achievable ligands; and c) prohibit arbitrarily large ligands. The bounds set determine the range of ligand geometries permissible. In this work, three sets of bounds were examined, as described in Table S1.

Table S1. The maximum length in Å of each geometric parameter, across three sets of geometric bounds.

	l_1 / central l_2 / outer l_2	Central r_1	Central r_2	Outer r_1 / outer r_2	Central r_3 / outer r_3
Set I: simplest ligands (no fragments may contain fused or connected rings)	5.0	1.4	1.4	1.4	1.4
Set II: intermediate complexity (up to four rings on the central fragment only)		2.8	3.5	1.4	
Set III: most difficult (large ring groups permitted throughout)		5.0	5.0	5.0	

For example, a fragment of 1.4Å radius approximates a benzene ring. Moreover, this schema also permits very simple ligands, such as two connected carboxylate groups with no intermittent rings, by permitting the fragment radii and inter-fragment distances to shrink to zero. It should also be noted that to maintain symmetry of ligands, only 2-c fragments are permitted to be elliptical (*i.e.*, r_1 not equal to r_2).

Optimization runs are initialized with a random ligand selected by choosing random values for each of the nine geometrical parameters. Each combination of fragments is optimized ten times, with each random starting ligand chosen such that it shares no geometrical parameters with any previous starting ligands.

Optimization results

In total, 22 fragment combinations were examined, of which 12 also permitted interpenetration; these were treated as separate optimizations, each of which was performed ten times, for a total of 340 optimizations for each set of geometric bounds. The maximum gravimetric methane-accessible surface area achieved using alchemical ligands across each of the ten runs was selected as the best result for each combination. The 34 optimum methane-accessible surface area values achieved for each param-

eter set as described in Table S1 are presented in Table S2 to Table S7. Results for interpenetrated structures are given in parentheses, and are zero where interpenetration was not achievable. Values for nitrogen-accessible surface area are also provided in italics. N/A indicates a fragment combination that was not examined. The best result for each net is highlighted in bold.

Table S2. The maximum methane-accessible gravimetric surface area (m^2g^{-1}) for each net incorporating two types of alchemical ligand; set I.

Central fragment	Side fragment	2-c	
			
2-c		8790 (8796.26) *8345.2 (8439.71)*	7834.64 (8480.25) *7597.9 (8157.34)*
		**9673.99** (9401.8) *9421.84 (9113.45)*	8096.22 (7591.19) *7965.29 (7476.09)*

Table S3. The maximum methane-accessible gravimetric surface area (m^2g^{-1}) for each net incorporating one type of alchemical ligand; set I.

Central fragment	Side fragment	2-c		3-c	
					
2-c		7750.45 (7770.66) *7424.2 (7220.84)*	7818.14 (7079.35) *7429.64 (6485.51)*	5824.48 (0) *5749.75 (0)*	5824.48 (0) *5749.75 (0)*
		**9021.72** (8590.98) *8847.97 (8392.92)*	8788.91 (8140.06) *8594.26 (6995.2)*	**5959.05** (0) *5914.53 (0)*	5943.99 (0) *5946.01 (0)*
3-c		7817.09 (7822.21) *7590.74 (6187.86)*	7805.58 (7834.17) *7599.52 (7626.5)*	5259.61 (0) *5267.24 (0)*	5259.61 (0) *5267.24 (0)*
		**8470.43** (8468.17) *8350.72 (8361.35)*	7816.69 (8139.08) *7590.37 (8036.26)*	**5355.93** (0) *5411.39 (0)*	5303.01 (0) *5321.87 (0)*
4-c		**7229.64** (0) *7055.14 (0)*	**7229.64** (0) *7055.14 (0)*	N/A (N/A)	N/A (N/A)

Table S4. The maximum methane-accessible gravimetric surface area (m^2g^{-1}) for each net incorporating two types of alchemical ligand; set II.

Central fragment \ Side fragment		2-c	
			
2-c		9112.97 (9172.07) *8749.3 (8749.23)*	8806.95 (8357.04) *8557.46 (8169.33)*
		**10760.3** (10512.4) *10275.1 (10060)*	10206.8 (9733.83) *9882.39 (9570.39)*

Table S5. The maximum methane-accessible gravimetric surface area (m^2g^{-1}) for each net incorporating one type of alchemical ligand; set II.

Central fragment \ Side fragment		2-c		3-c	
					
2-c		8215.64 (8161.07) *7857.45 (7588.34)*	8235.47 (8066.98) *7884.39 (7644.3)*	6271.65 (0) *6222.19 (0)*	6271.65 (0) *6222.19 (0)*
		**9978** (9447.58) *9519.32 (9111.19)*	8819.87 (9329.51) *8542.64 (8904.22)*	6305.36 (0) *6309.48 (0)*	**6318.89** (0) *6254.59 (0)*
3-c		8253.08 (8249.47) *8004.99 (7999.93)*	7773.31 (7759.54) *7669.49 (7663.5)*	5869.12 (0) *5848.58 (0)*	5869.12 (0) *5848.58 (0)*
		**9539.93** (9478.94) *9226.83 (9177.53)*	8456.88 (8460.6) *8539.62 (8533.01)*	**6225.84** (0) *6180.23 (0)*	6051.89 (0) *6044.25 (0)*
4-c		**7229.64** (0) *7055.14 (0)*	6718.71 (0) *6886.04 (0)*	N/A (N/A)	N/A (N/A)

Table S6. The maximum methane-accessible gravimetric surface area (m^2g^{-1}) for each net incorporating two types of alchemical ligand; set III.

Central fragment \ Side fragment		2-c	
			
2-c		10215.7 (10325.3) *9734.27 (9883.38)*	10496.8 (10406) *10035.1 (10057.9)*
		**11006.5** (10824.3) *10509.7 (10345.8)*	10832.5 (10900.3) *10455.3 (10467.5)*

Table S7. The maximum methane-accessible gravimetric surface area (m^2g^{-1}) for each net incorporating one type of alchemical ligand; set III.

Central fragment \ Side fragment		2-c		3-c	
					
2-c		9425.86 (9452.72) *9009.48 (9027.02)*	9656.04 (9645.19) *9214.77 (9223.43)*	7751.73 (0) *7597.04 (0)*	8005.39 (0) *7936.79 (0)*
		**10513.7** (10495) *10040.9 (10037.9)*	10462.3 (10438.3) *9960.69 (9983.18)*	**8534.09** (0) *8307.01 (0)*	8509.44 (0) *8367.34 (0)*
3-c		9053.94 (8997.43) *8759.88 (8714.63)*	9119.92 (8938.19) *8919.08 (8808.51)*	7396.98 (0) *7306.58 (0)*	7995.33 (0) *7984.03 (0)*
		9735.42 (**9842.02**) *9395.08 (9471.02)*	9543.71 (9189.18) *9188.95 (8904.65)*	7987 (0) *7846.93 (0)*	**8196.53** (0) *8103.58 (0)*
4-c		8993.22 (0) *8692.72 (0)*	**9549.47** (0) *9371.55 (0)*	N/A (N/A)	N/A (N/A)

The specific geometrical parameters leading to each of the best ligands are provided in Table S8 to Table S10; for **pcu** (two ligand) nets, the nitrogen-terminated ligands' parameters are given in parentheses.

Table S8. Geometrical parameters for the best alchemical ligands achieved for each net; set I.

	l_1	Central r_1	Central r_2	Side r_1	Side r_2	Central l_2	Central r_3	Side l_2	Side r_3
pcu (two ligands)	5 (4.4)	1.4 (1.4)	1.4 (1.4)	1.4 (1.4)	0.9 (0.9)	5 (5)	0.4 (0.7)	1.9 (2.3)	0.2 (0.5)
pcu	5	1.4	1.4	1.4	0.9	5	0.7	4.6	1.2
fof	5	1.4	1.4	1.4	1.4	1.2	0	2.4	0
tbo	5	1.4	1.4	1.4	0.9	5	0.7	3.4	0.4
rht	5	1.4	1.4	1.4	1.4	1.9	0.3	3.3	0.2
pts	5	1.4	1.1	1.4	1.4	1.8	0.3	3.4	1.4

Table S9. Geometrical parameters for the best alchemical ligands achieved for each net; set II.

	l_1	Central r_1	Central r_2	Side r_1	Side r_2	Central l_2	Central r_3	Side l_2	Side r_3
pcu (two ligands)	5 (4.9)	2.6 (2.8)	3.2 (3.1)	1.4 (1.4)	0.9 (0.9)	5 (5)	1.1 (1.2)	2.5 (1.5)	0.3 (1)
pcu	5	2.8	3.2	1.4	0.9	4.7	1.0	3.2	0.3
fof	5	2.8	1.9	1.4	1.4	0.7	0	0	0
tbo	5	2.1	3.2	1.4	0.9	5	1.4	2.6	0.4
rht	5	2.8	3.5	1.4	1.4	2.1	0.2	2.4	1.3
pts	5	2.8	1.1	1.4	1.4	1.8	0.7	2.6	1.3

Table S10. Geometrical parameters for the best alchemical ligands achieved for each net; set III.

	l_1	Central r_1	Central r_2	Side r_1	Side r_2	Central l_2	Central r_3	Side l_2	Side r_3
pcu (two ligands)	4.4 (5)	2.5 (3)	4.1 (3.5)	4.7 (5)	0.9 (0.9)	5 (5)	0.9 (1.4)	0.1 (4.6)	1 (1.3)
pcu	5	4.6	2.5	5	0.9	5	1.4	0.3	0.6
fof	5	4.9	3	2.3	5	5	0.1	3.2	0.4
tbo	4.9	2.6	3.6	3.1	0.9	5	1.4	4.9	0.6
rht	5	5	3.3	5	5	5	0.4	2.5	0.1
pts	5	5	2.5	5	4.9	0	0.5	3.2	0.4

For each of the three parameter bounds, the alchemical ligands for the overall highest and lowest surface area topologies, **pcu** (two ligands) and **rht** respectively, were translated into real molecules enabling the computation of the corresponding gravimetric surface area (presented in the manuscript). The projected ligands for the rht net are presented in the manuscript, and those for the pcu (two ligands) net are presented in Figure S2 to Figure S4.

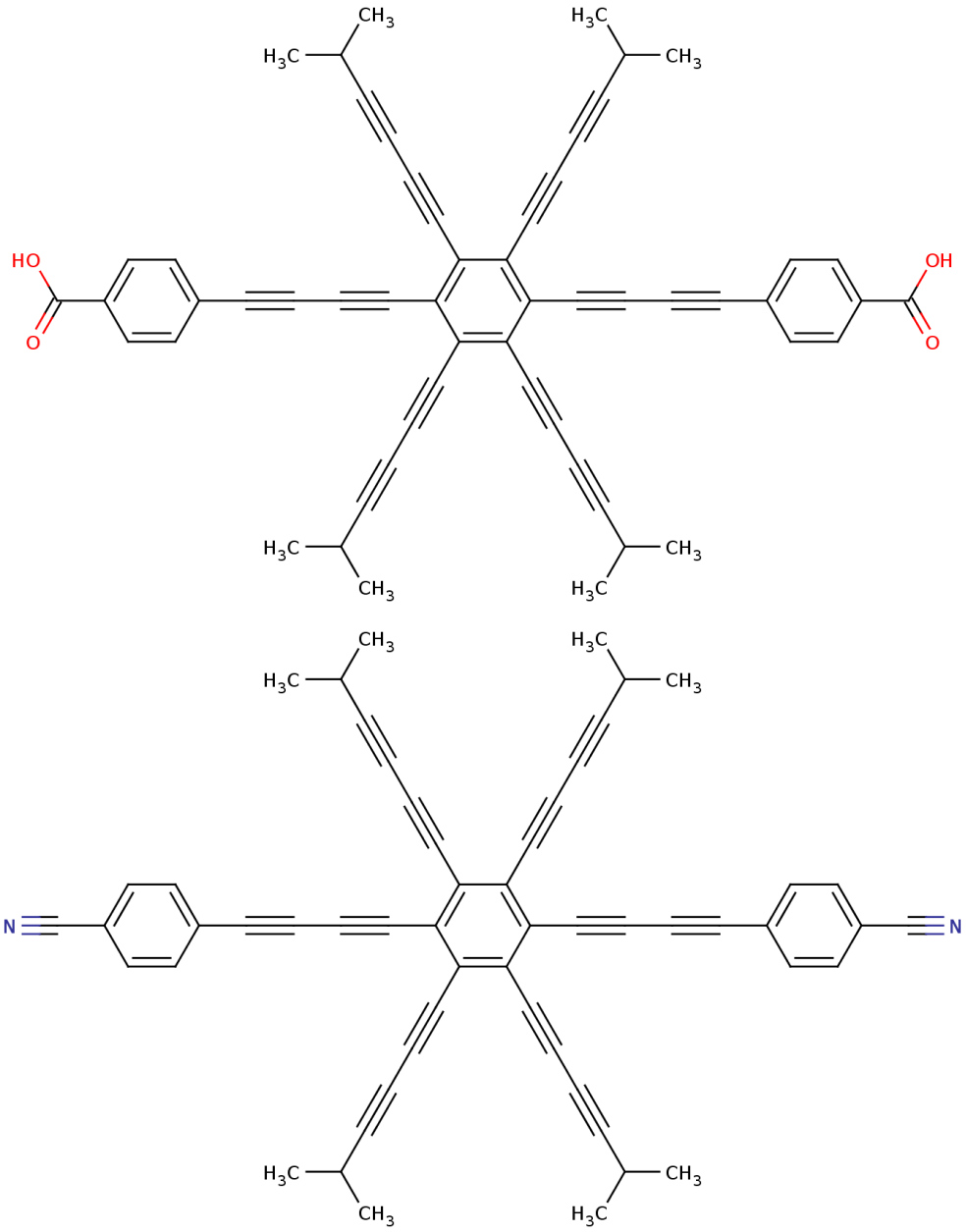

Figure S2. The real ligands projected from the highest surface area alchemical ligands for the **pcu** (two ligands) net; set I.

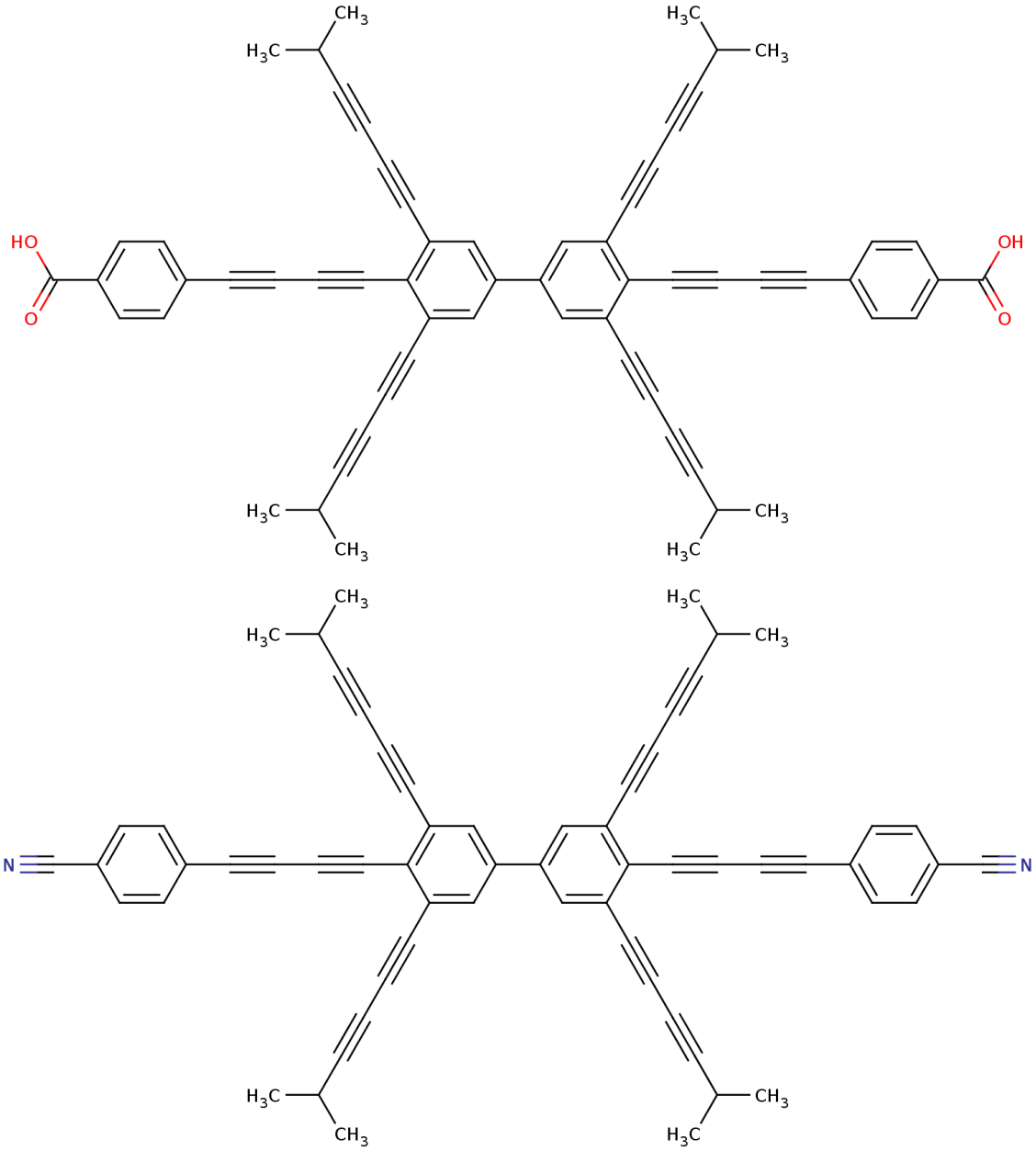

Figure S3. The real ligands projected from the highest surface area alchemical ligands for the **pcu** (two ligands) net; set II.

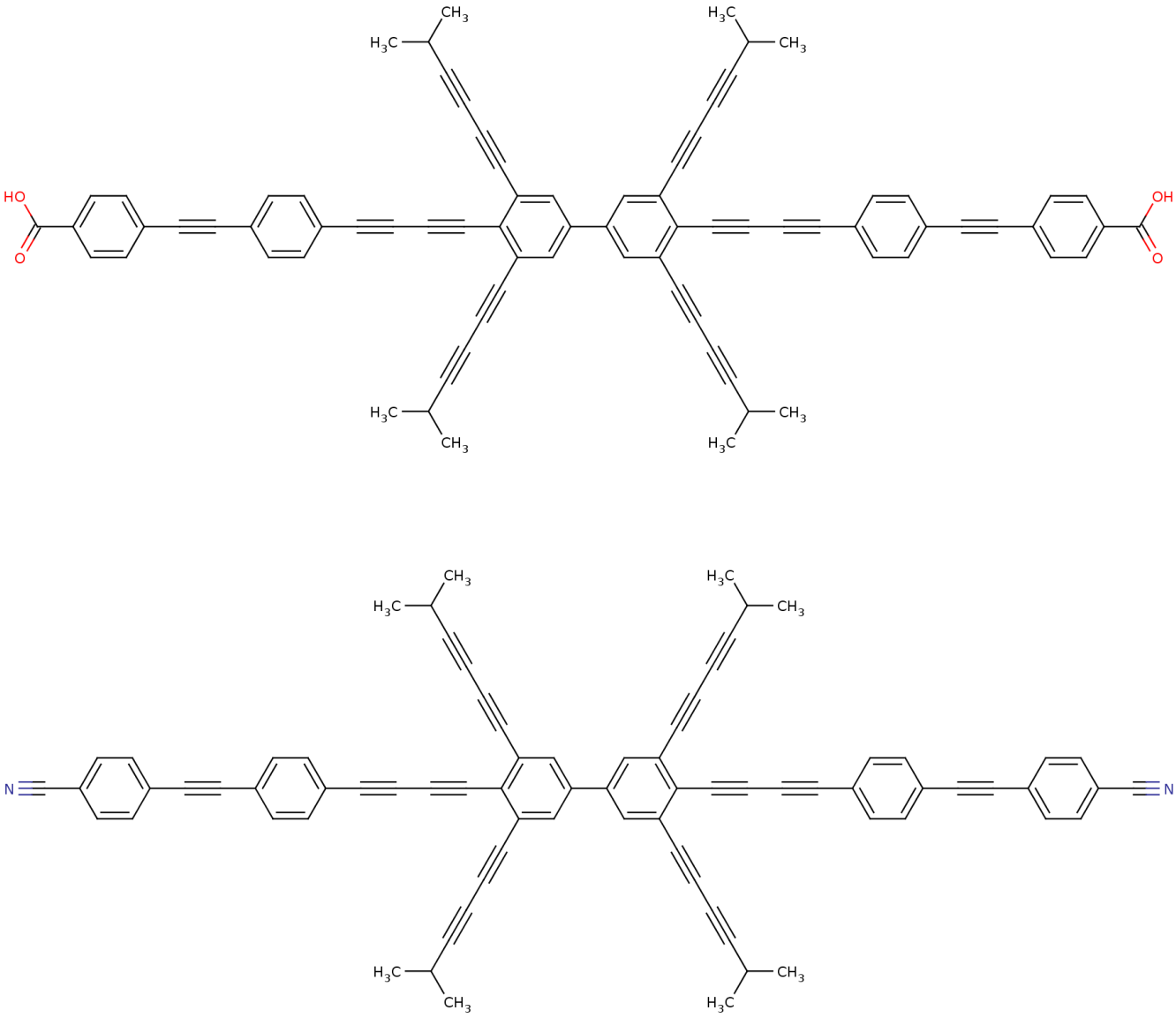

Figure S4. The real ligands projected from the highest surface area alchemical ligands for the **pcu** (two ligands) net; set III.