Electronic Supplementary Material (ESI) for CrystEngComm.
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Supplementary Information

Comparing the host behaviour of *N,N'*-bis(9-phenyl-9-thioxanthenyl)ethylenediamine and *N,N'*-bis(9-phenyl-9-xanthenyl)ethylenediamine in the presence of various alkylated aromatic and aniline guests: crystal engineering considerations

Benita Barton,*[1] Lize de Jager*[2] and Eric C. Hosten

Department of Chemistry, PO Box 77000, Nelson Mandela University, Port Elizabeth, 6031, South Africa.

*E-mail: *[1]benita.barton@mandela.ac.za; *[2]s213337665@mandela.ac.za*

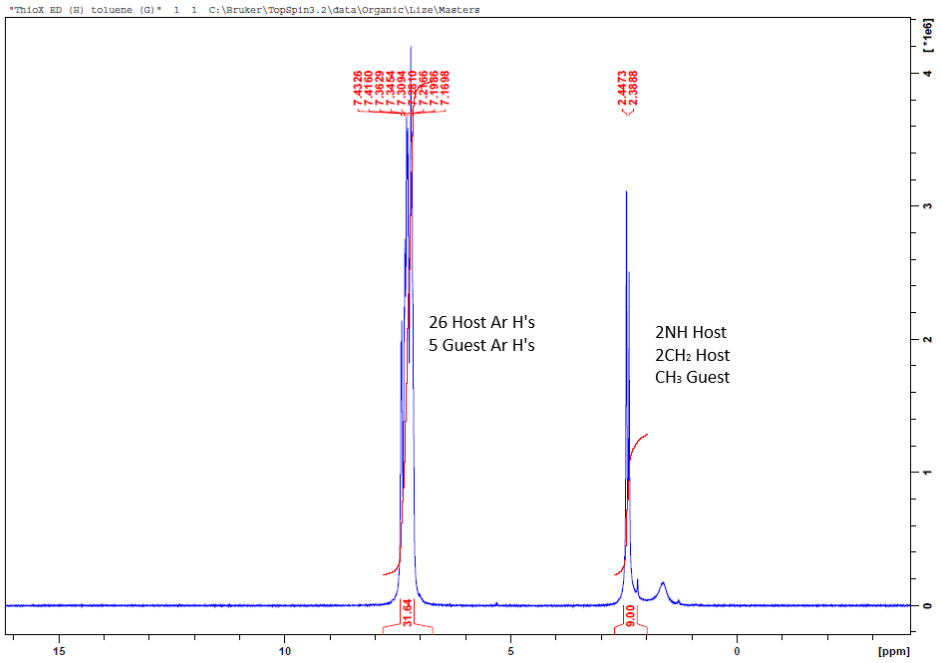


Figure S1a. [1]H-NMR spectrum for the complex between TOL and $\mathbf{H_1}$.

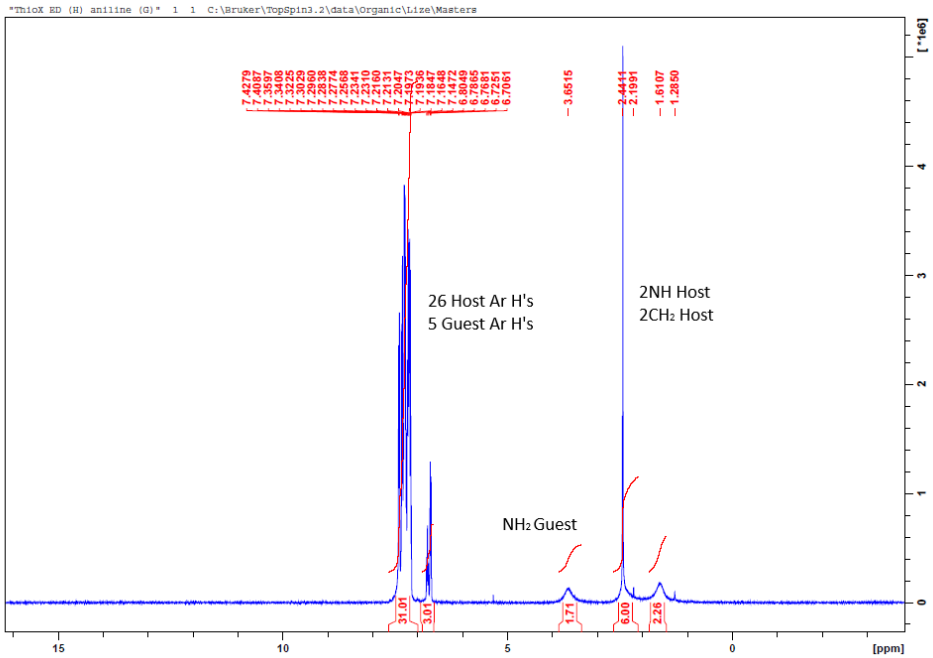


Figure S1b. [1]H-NMR spectrum for the complex between ANI and $\mathbf{H_1}$.

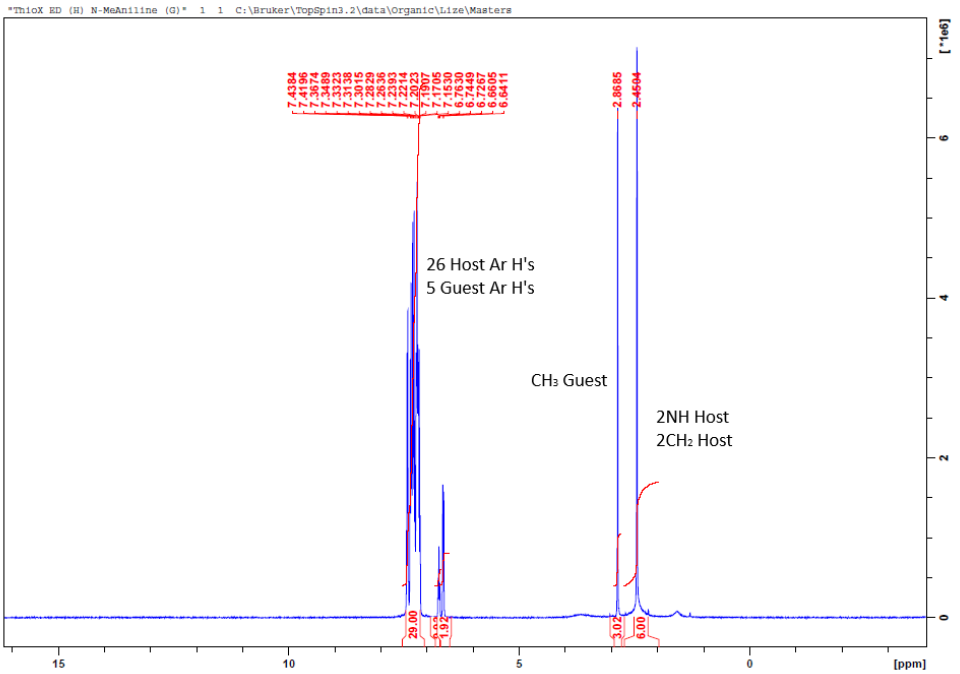


Figure S1c. ^{1}H-NMR spectrum for the complex between NMA and $\mathbf{H_1}$.

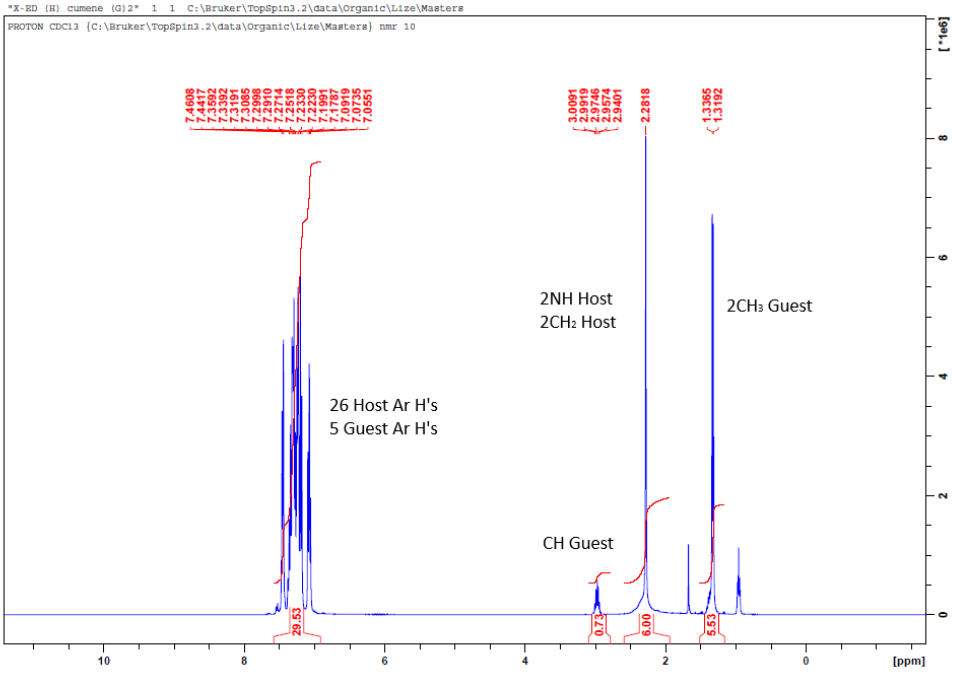


Figure S1d. ^{1}H-NMR spectrum for the complex between CU and $\mathbf{H_2}$.

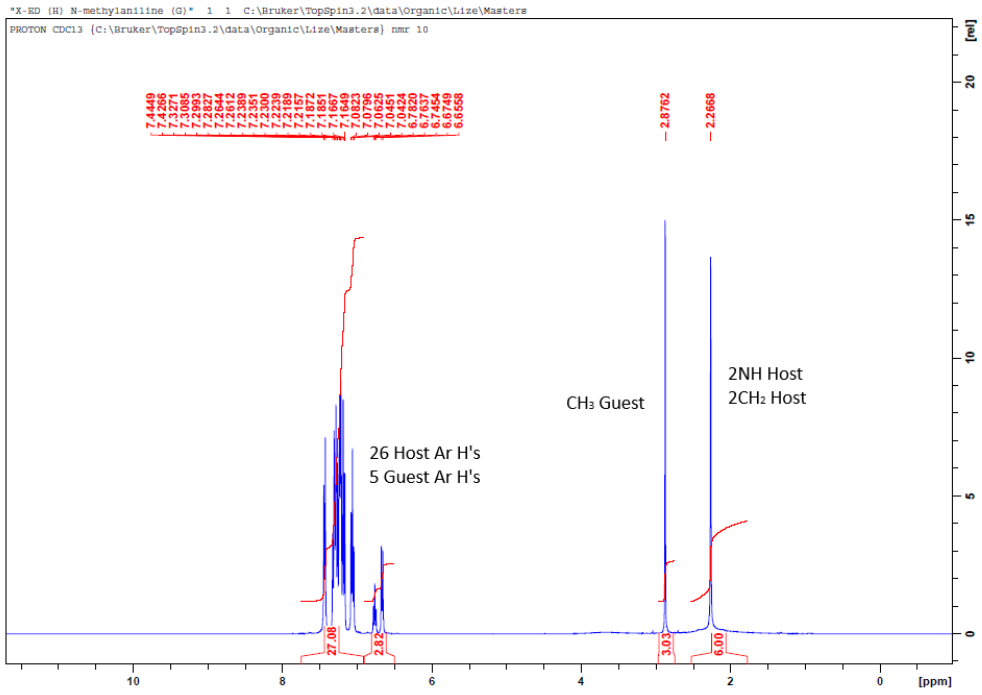


Figure S1e. ^{1}H-NMR spectrum for the complex between NMA and **H_2**.

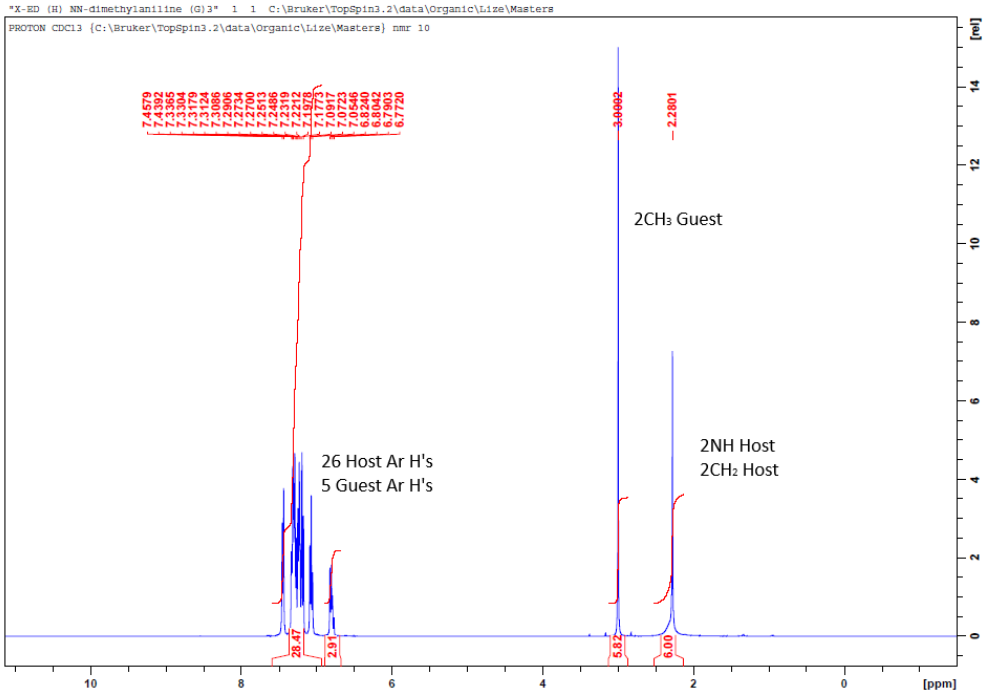


Figure S1f. ^{1}H-NMR spectrum for the complex between NNDMA and **H_2**.

Table S2. Duplicate data for equimolar competition experiments of ANI, NMA and NNDMA with $\mathbf{H_1}$

Comp:	Batch 1	Batch 2	Average	% e.s.d.s
ANI + NMA	90.00:10.00	88.24:11.76	89.12:10.88	(0.88): (0.88)
ANI + NNDMA	93.77: 6.23	90.69:9.31	92.23:7.77	(1.54): (1.54)
NMA + NNDMA	[a]	[a]	-	-
ANI + NMA + NNDMA	89.50:5.73:4.78	88.90:5.91:5.20	89.20:5.82:4.98	(0.30): (0.09):(0.21)

[a]No inclusion occurred.

Table S3. Duplicate data for equimolar competition experiments of TOL, EB and CU with $\mathbf{H_1}$

Comp:	Batch 1	Batch 2	Average	% e.s.d.s
TOL + EB	92.07:7.94	91.44:8.54	91.76:8.24	(0.31): (0.31)
TOL + CU	96.77:3.24	96.13:3.87	96.44:3.56	(0.32): (0.32)
EB + CU	62.09:37.91	63.70:36.30	62.90:37.10	(0.81):(0.81)
TOL + EB + CU	89.08:8.74:2.18	90.50:7.70:1.80	89.90:8.22:1.88	(0.71): (0.52):(0.19)

Table S4. Duplicate data for equimolar competition experiments of ANI, NMA and NNDMA with $\mathbf{H_2}$

Guests:	Batch 1	Batch 2	Average	% e.s.d.s
ANI + NMA	24.03:75.97	21.74:78,26	22.89:77.12	(1.15): (1.15)
ANI + NNDMA	1.35:98.65	1.28:98.72	1.32:98.69	(0.03): (0.03)
NMA + NNDMA	7.57:92.43	5.77:94.23	6.67:93.33	(0.90):(0.90)
ANI + NMA + NNDMA	1.99:5.99:92.01	5.38:6.17:88.46	3.69:6.08:90.24	(1.70): (0.09):(1.78)

Table S5. Duplicate data for equimolar competition experiments of TOL, EB and CU with $\mathbf{H_2}$

Guests:	Batch 1	Batch 2	Batch 3	Average	% e.s.d.s
TOL + EB	[a]	[a]	[a]	-	-
TOL + CU	[a]	[a]	[a]	-	-
EB + CU	49.19:50.81	46.51:53.50	49.98:50.02	48.56:51.44	(1.48);(1.48)
TOL + EB + CU	[a]	[a]	[a]	-	-

[a]No inclusion occurred

Table S6. K values for competition experiment of ANI/NMA with **H_1**.

ANI ml	ANI c	NMA ml	NMA c	K values
1	1	0	0	
0,74531	0,92048	0,25469	0,07952	3,95560512
0,5402	0,94585	0,4598	0,05415	14,8675085
0,43038	0,91012	0,56962	0,08988	13,4019731
0,34044	0,90494	0,65956	0,09506	18,4431757
0,14723	0,02795	0,85277	0,97205	0,16654393
0	0	1	1	10,1669613

Table S7. K values for competition experiment of ANI/NNDMA with **H_1**.

ANI ml	ANI c	NNDMA ml	NNDMA c	K values
1	1	0	0	
0,7598	0,93357	0,2402	0,06643	4,44279576
0,57566	0,90274	0,42434	0,09726	6,84189397
0,47608	0,91477	0,52392	0,08523	11,811484
0,34071	0,86149	0,65929	0,13851	12,0354053
0,22098	0,70008	0,77902	0,29992	8,22882605
0	0	1	1	8,67208101

Table S8. K values for competition experiment of ANI/NNDMA with **H_2**.

NNDMA ml	NNDMA c	ANI ml	ANI c	K value
1	1	0	0	
0,84303	0,98557	0,15697	0,01443	12,7172958
0,63608	0,96269	0,36392	0,03731	14,7623465
0,56845	0,93178	0,43155	0,06822	10,369087
0,41709	0,94891	0,58291	0,05109	25,9573796
0,23338	0,60841	0,76662	0,39159	5,10365443
0	0	1	1	13,7819527

Table S9. K values for competition experiment of NMA/NNDMA with **H_2**.

NNDMA ml	NNDMA c	NMA ml	NMA c	K value
1	1	0	0	
0,81391	0,96842	0,18609	0,03158	7,01129557
0,61555	0,93217	0,38445	0,06783	8,5832119
0,5	0,93524	0,5	0,06476	14,4416306
0,43407	0,43577	0,56593	0,56423	1,00694117
0,20745	0,04099	0,79255	0,95901	0,16329317
0	0	1	1	6,24127449

Table S10. K values for competition experiment of ANI/NMA with H_2.

NMA ml	NMA c	ANI ml	ANI c	K value
1	1	0	0	
0,84382	0,94534	0,15618	0,05466	3,20106145
0,63729	0,80534	0,36271	0,19466	2,35464249
0,5147	0,79952	0,4853	0,20048	3,76022993
0,46543	0,75464	0,53457	0,24536	3,53253333
0,22835	0,18754	0,77165	0,81246	0,78002993
0	0	1	1	2,72569943

Table 11. K values for competition experiment of TOL/EB with H_1.

TOL ml	TOL c	EB ml	EB c	K value
1	1	0	0	
0,74434	0,96978	0,25566	0,03022	11,0222483
0,55354	0,92547	0,44646	0,07453	10,0153186
0,43868	0,91253	0,56132	0,08747	13,3490607
0,34253	0,87077	0,65747	0,12923	12,9335409
0,18537	0,21562	0,81463	0,78438	1,20804602
0	0	1	1	9,70564289

Table 12. K values for competition experiment of TOL/CU with H_1.

TOL ml	TOL c	CU ml	CU c	K value
1	1	0	0	
0,73171	0,98423	0,26829	0,01577	22,8839189
0,48083	0,9712	0,51917	0,0288	36,4111351
0,40474	0,96633	0,59526	0,03367	42,2097635
0,3137	0,94882	0,6863	0,05118	40,5586069
0,16365	0,51494	0,83635	0,48506	5,42541817
0	0	1	1	29,4977685

Table 13. K values for competition experiment of EB/CU with H_1.

EB ml	EB c	CU ml	CU c	K value
1	1	0	0	
0,77593	0,87745	0,22407	0,12255	2,06761766
0,54517	0,70261	0,45483	0,29739	1,97108394
0,4639	0,63175	0,5361	0,36825	1,982549
0,35935	0,5158	0,64065	0,4842	1,89915204
0,18003	0,2538	0,81997	0,7462	1,54913567
0	0	1	1	1,89390766

Table S14. K values for competition experiment of CU/EB with H_2.

CU ml	CU c	EB ml	EB c	K value
1	1	0	0	
0,78946	0,8187	0,21054	0,1813	1,20429109
0,55886	0,62882	0,44114	0,37118	1,33725796
0,47916	0,50022	0,52084	0,49978	1,08794253
0,36782	0,35244	0,63218	0,64756	0,93542848
0,19814	0,15228	0,80186	0,84772	0,72697057
0	0	1	1	1,05837813

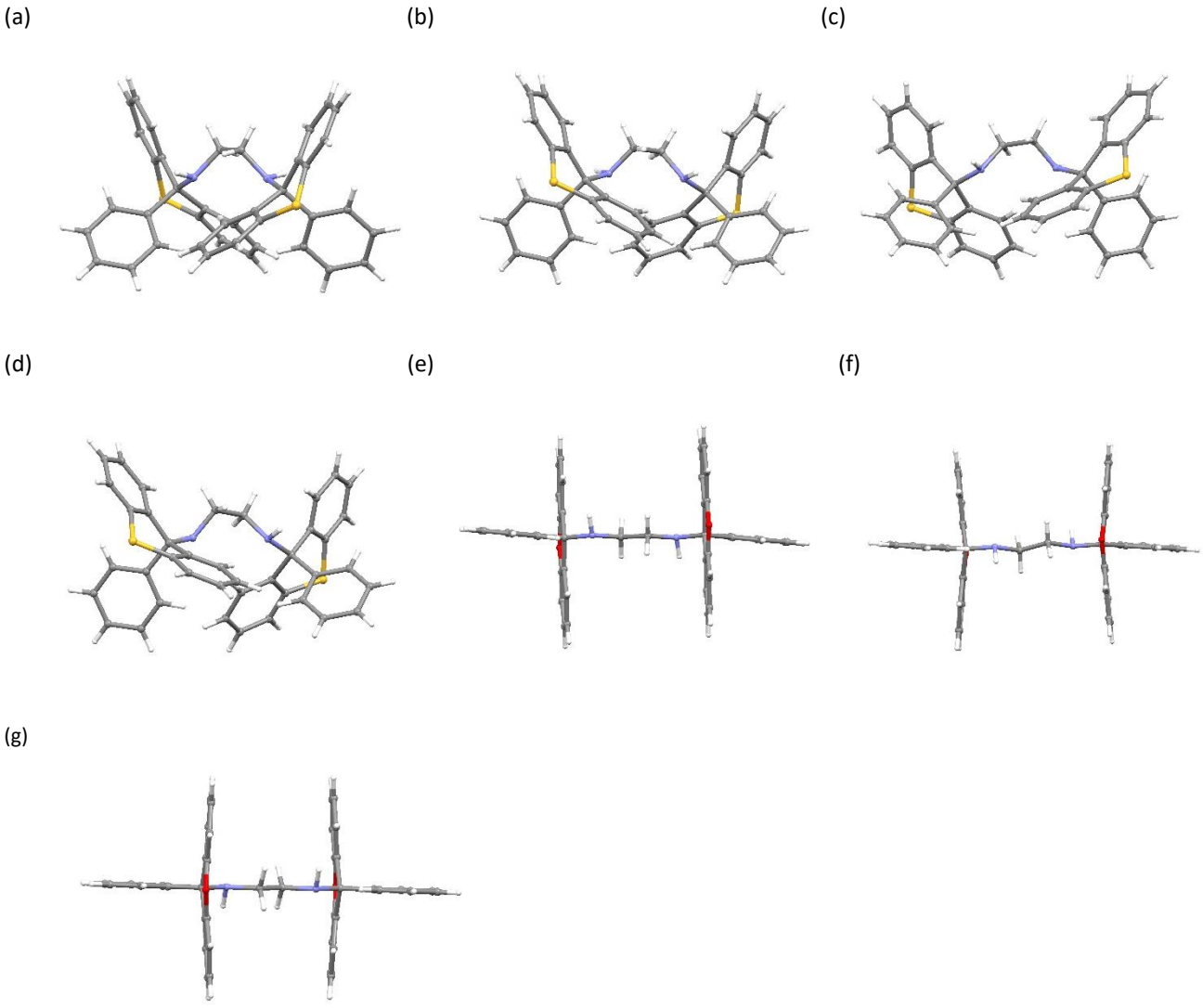
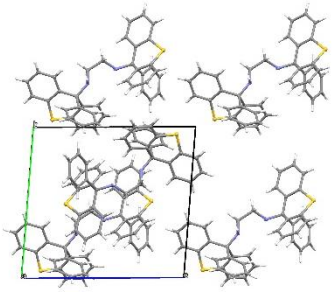
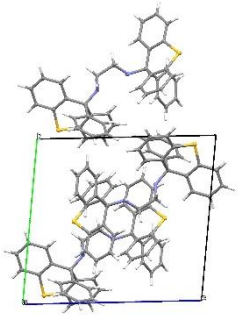


Figure S15. Host geometry in complexes (a) H_1·TOL, (b) H_1·EB, (c) H_1·ANI, (d) H_1·NMA, (e) H_2·CU, (f) H_2·NMA and (g) H_2·NNDMA; guests were removed for ease of examination.

(a)



(b)



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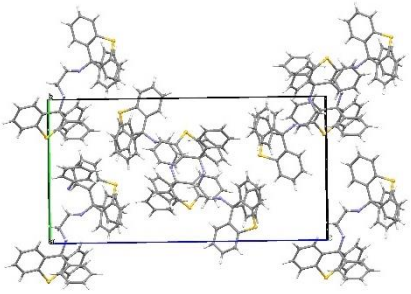
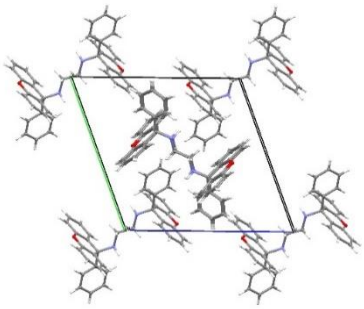
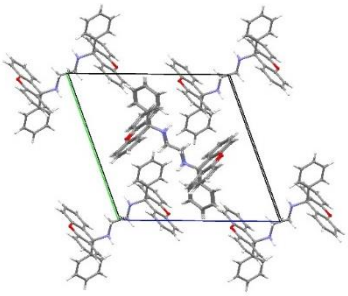


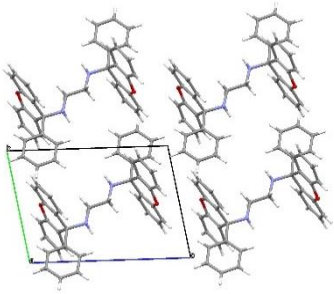
(d)



(e)



(f)



(g)

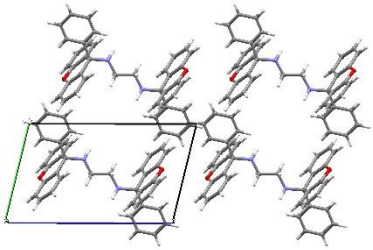


Figure S16. Host packing in complexes (a) **H₁**·TOL, (b) **H₁**·EB, (c) **H₁**·ANI, (d) **H₁**·NMA, (e) **H₂**·CU, (f) **H₂**·NMA and (g) **H₂**·NNDMA; guests were removed for ease of examination.

Table S17. Crystallographic data for **H$_1$**·TOL and **H$_1$**·EB.[a]

Non-covalent interaction	**H$_1$**·TOL	**H$_1$**·EB	Symmetry
π···π (H···H and H···G)	4.361(1) – 5.919(1) Å 5.045(1) – 5.919(1) Å [8]	4.521(1) – 5.997(1) Å 4.999(1) – 5.997(1) Å [7]	
CH···π (host-host)			
$C_{(host)}$–H_{32}···$Cg_{(host)}$	2.80 Å, 134°		x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.71 Å, 147°		3/2–x, –1/2+y, 1/2–z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.84 Å, 138°		x, 1+y, z
$C_{(guest)}$–$H_{(guest)}$···$Cg_{(host)}$	2.66 Å, 162°		3/2–x, –1/2+y, 1/2–z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$		2.96 Å, 139°	x, y,1+z
$C_{(guest)}$–$H_{(guest\ 1)}$···$Cg_{(host)}$		2.99 Å, 155°	1+x, y, –1+z
$C_{(guest)}$–$H_{(guest\ 2)}$···$Cg_{(host)}$		2.88 Å, 163°	1+x, y, –1+z
H-bonding (intramolecular)	Non-classical	Non-classical	
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.64(2) Å, 103°	2.761(2) Å, 103°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	3.443(2) Å, 152°	3.432(2) Å, 154°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.906(2) Å, 102°	2.904(2) Å, 102°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$		3.456(2) Å, 151°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.766(2) Å, 103°	2.764(2) Å, 103°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.897(2) Å, 102°	2.899(2) Å, 102°	x, y, z
Other short contacts (host/ guest and guest/guest)			
$C_{(host)}$–$H_{(host)}$···$H_{(guest)}$–$C_{(guest)}$	2.35Å, 138°(<)		3/2–x, 1/2+y, 1/2–z
$C_{(host)}$–$H_{(host)}$···$H_{(guest)}$–$C_{(guest)}$	2.37Å, 129°(<)		x, y, z
$C_{(host)}$–$H_{(host)}$···$C_{(host)}$–$C_{(host)}$		2.86 Å, 145° (<)	–x, 1–y, 1–z
$C_{(guest\ 2)}$–$C_{(guest\ 2)}$···$H_{(guest\ 2)}$–$C_{(guest\ 2)}$		1.89 Å, 131° (<<)	2–x, 1–y, –z

[a]Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved while those denoted by << is this sum minus 0.2 Å.

Table S18. Crystallographic data for **H$_1$**·ANI and **H$_1$**·NMA.[a,b]

Non-covalent interaction	**H$_1$**·ANI	**H$_1$**·NMA	Symmetry
π···π (H···H and H···G) H···G major H···G minor	4.379(1) –5.935(3) Å 4.885(1) – 5.927(1) Å [7] 4.714(5) – 5.935(3) Å [8]	4.658(1) – 5.932(1) Å 4.935(1) – 5.893 (1) Å [7]	
CH···π (host-host)			
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.78 Å, 134°		x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.71 Å, 149°		3/2–x, –1/2+y, 1/2–z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.84 Å, 137°		x, 1+y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.93 Å, 133°		x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$		2.94 Å, 139°	x, y, 1+z
$C_{(guest)}$–$H_{(guest)}$···$Cg_{(host)}$		2.93 Å, 140°	–x, 1–y, 1–z
X–Y···π (guest-host)			
$C_{(guest)}$–$N_{(guest)}$···$Cg_{(host)}$	3.518 (4) Å, 109°		2–x, 1–y,1–z
H-bonding (Intramolecular)	Non-classical	Non-classical	
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.766(2) Å, 103°	2.767(2) Å, 103°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	3.436(2) Å, 152°	3.466(2) Å, 158°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.913(2) Å, 102°	2.910(2) Å, 102°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$		3.454(2) Å, 148°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.775(2) Å, 103°	2.768(2) Å, 103°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.896(2) Å, 102°	2.900(2) Å, 102°	x, y, z
Other short contacts (host/ guest and guest/guest)			
$C_{(host)}$–$H_{(host)}$···$C_{(host)}$–$C_{(host)}$	2.89Å, 153°(<)		x, 1+y, z
$C_{(host)}$–$H_{(host)}$···$H_{(guest\ 1)}$–$C_{(guest\ 1)}$	2.34Å, 134°(<)		–1/2+x, ½-y, –1/2+z
$C_{(host)}$–$H_{(host)}$···$H_{(guest\ 2)}$–$C_{(guest\ 2)}$	2.30Å, 149°(<)		–1/2+x, 1/2–y, -1/2+z
$C_{(guest\ 2)}$–$N_{(guest\ 2)}$···$N_{(guest\ 2)}$–$C_{(Guest\ 2)}$	2.3890Å, 125.1(6)°(<<)		2–x, –y, 1–z
$C_{(guest\ 2)}$–$H_{(guest\ 2)}$···$H_{(host)}$–$C_{(host)}$	2.35Å, 138°(<)		1–x, 1–y, 1-z
$C_{(guest\ 2)}$–$N_{(guest\ 2)}$···$C_{(host)}$–$C_{(host)}$	3.244Å, 105.5(2)°(<)		x, 1+y, z
$C_{(host)}$–$H_{(host)}$···$H_{(guest\ 1)}$–$C_{(guest\ 1)}$		2.37 Å, 143° (<)	x,1+y,1+z

[a]Number of H-G interactions indicated in parentheses.

[b]Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved while those denoted by << is this sum minus 0.2 Å.

Table S19. Crystallographic data for **H_2**·CU.[a]

Non-covalent interaction	**H_2**·CU	Symmetry
π···π (H···H and H···G)	3.981(1)−5.977(1) Å	
CH···π		
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.85 Å, 90°	x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.96 Å, 84°	x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.99 Å, 80°	x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.74 Å, 94°	x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.94 Å, 143°	x, −1+y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(guest)}$	3.00 Å, 117°	−1+x, −1+y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.68 Å, 105°	x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.97 Å, 151°	1+x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.77 Å, 104°	x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.69 Å, 156°	1−x, 1−y, 1−z
H-bonding (intramolecular)	Non-classical	
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.790(3) Å, 102°	x, y, z
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.758 (3) Å, 102°	x, y, z
Otherhort contacts (host/guest and guest/guest)		
$C_{(host)}$–$C_{(host)}$···$H_{(host)}$–$C_{(host)}$	2.87 Å, 112° (<)	−x, 1−y, 1−z
$C_{(host)}$–$C_{(host)}$···$C_{(guest\ 1)}$–$C_{(guest\ 1)}$	3.33 Å, 112° (<)	−1+x, −1+y, z
$C_{(host)}$–$H_{(host)}$···$H_{(host)}$–$C_{(host)}$	2.35 Å, 131° (<)	x, y, z
$C_{(host)}$–$H_{(host)}$···$C_{(guest\ 1)}$–$C_{(guest\ 1)}$	2.88 Å, 131° (<)	1−x, 1−y, −z
$C_{(host)}$–$H_{(host)}$···$H_{(host)}$–$C_{(host)}$	2.78 Å, 101° (<)	−1+x, y, z
$C_{(guest\ 1)}$–$H_{(guest\ 1)}$···$C_{(host)}$–$O_{(host)}$	2.83 Å, 169° (<)	1+x, y, z
$C_{(guest\ 2)}$–$H_{(guest\ 2)}$···$C_{(host)}$–$O_{(host)}$	2.72 Å, 150° (<)	1−x, 1−y, 1−z

[a]Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved.

Table S20. Crystallographic data for **H_2**·NMA and **H_2**·NNDMA.[a]

Non-covalent interaction	**H_2**·NMA	**H_2**·NNDMA	Symmetry
π···π (H···H and H···G) H···G interactions	4.090(1)–5.930(1) Å 4.735(1)–5.930(1) Å [6]	3.919(2)–5.839(3) Å 4.977(3)–5.839(3) Å [8]	
CH···π (host-host)			
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.91 Å, 77°		x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.57 Å, 97°		x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(guest)}$	2.95 Å, 127°		x, 1+y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.61 Å, 163°		2–x, 2–y, 2–z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$	2.83 Å, 104°		x, y, z
$C_{(guest)}$–$H_{(guest)}$···$Cg_{(host)}$	2.89 Å, 139°		x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$		3.00 Å, 142°	x, –1+y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$		2.93 Å, 142°	1+x, y, z
$C_{(host)}$–$H_{(host)}$···$Cg_{(guest)}$		2.95 Å, 141°	1–x, 1–y,1–z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$		2.90 Å, 141°	1–x, 2–y, -z
$C_{(host)}$–$H_{(host)}$···$Cg_{(host)}$		2.57 Å, 106°	x, y, z
H-bonding (intramolecular)	Non-classical	Non-classical	
$C_{(host)}$–$H_{(host)}$···$N_{(host)}$	2.804(1) Å, 102°	2.770(2) Å, 103°	x, y, z
Other short contacts (host/ guest and guest/guest)			
$C_{(host)}$–$H_{(host)}$···$H_{(guest)}$–$C_{(guest)}$	2.32 Å, 144° (<)		2-x, 1–y, 1–z
$C_{(host)}$–$H_{(host)}$···$O_{(host)}$–$C_{(host)}$	2.64 Å, 165° (<)		1+x, 1+y, z
$C_{(host)}$–$H_{(host)}$···$C_{(host)}$–$C_{(host)}$		2.81 Å, 136° (<)	1–x, 2–y, -z
$N_{(host)}$–$H_{(host)}$···$H_{(guest)}$–$C_{(guest)}$		2.26 Å, 168° (<)	–1+x, 1+y, z
$C_{(host)}$–$H_{(host)}$···$C_{(guest)}$–$N_{(guest)}$		2.75 Å, 146° (<)	1–x, 1–y, 1–z

[a]Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved.

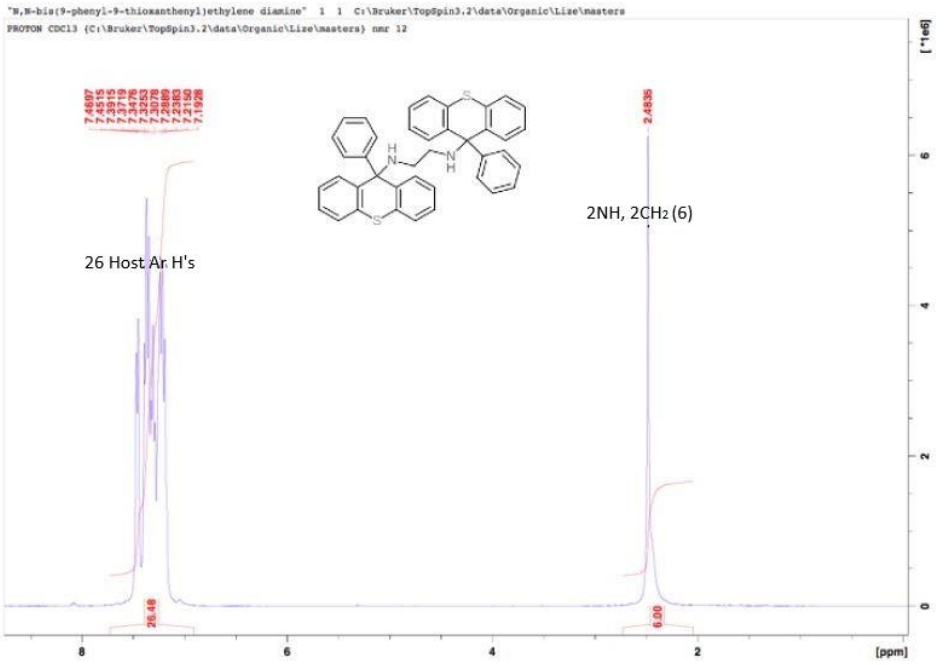


Figure S21a. ^{1}H-NMR spectrum for **H_1**.

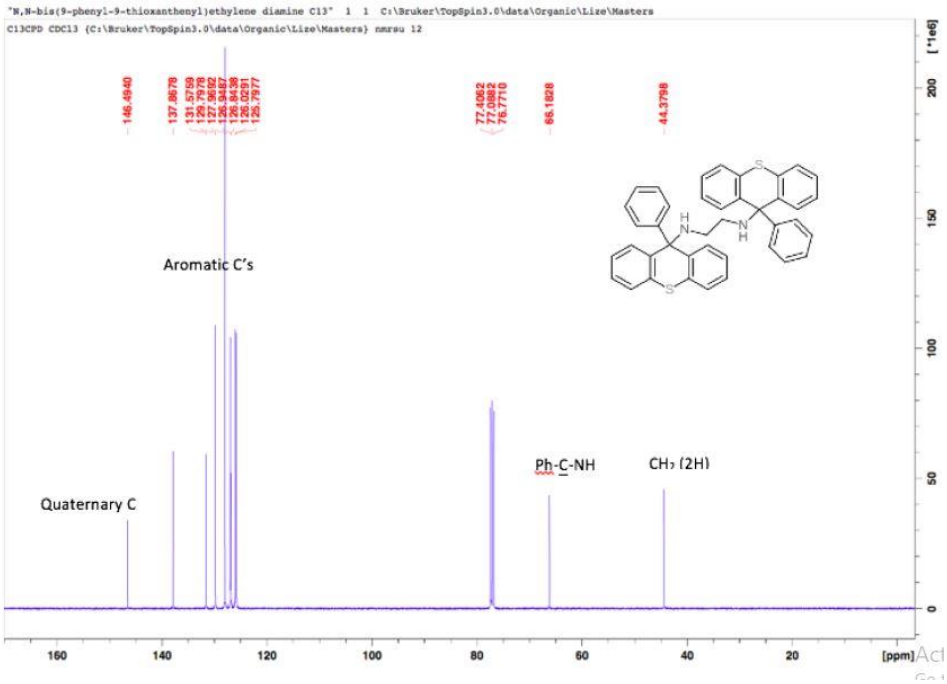


Figure S21b. ^{13}C-NMR spectrum for **H_1**.

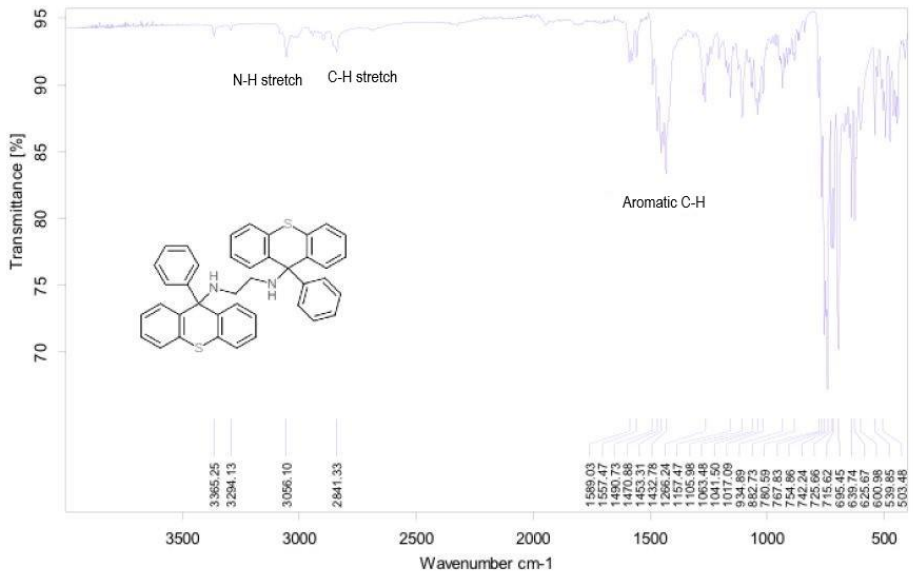


Figure S21c. IR spectrum for **H_1**.

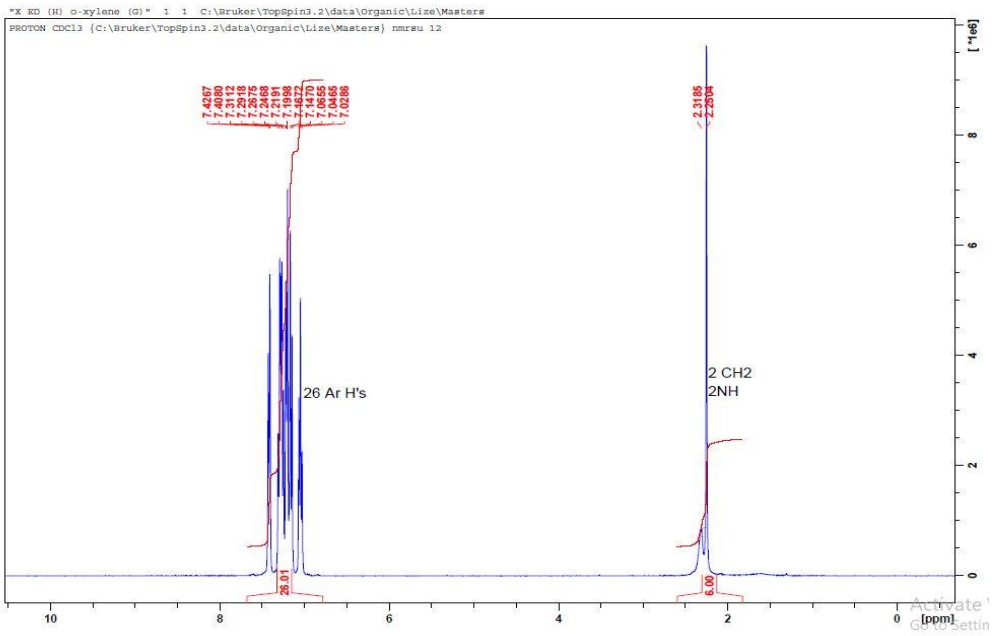


Figure S21d. ^{1}H-NMR spectrum for **H_2**.

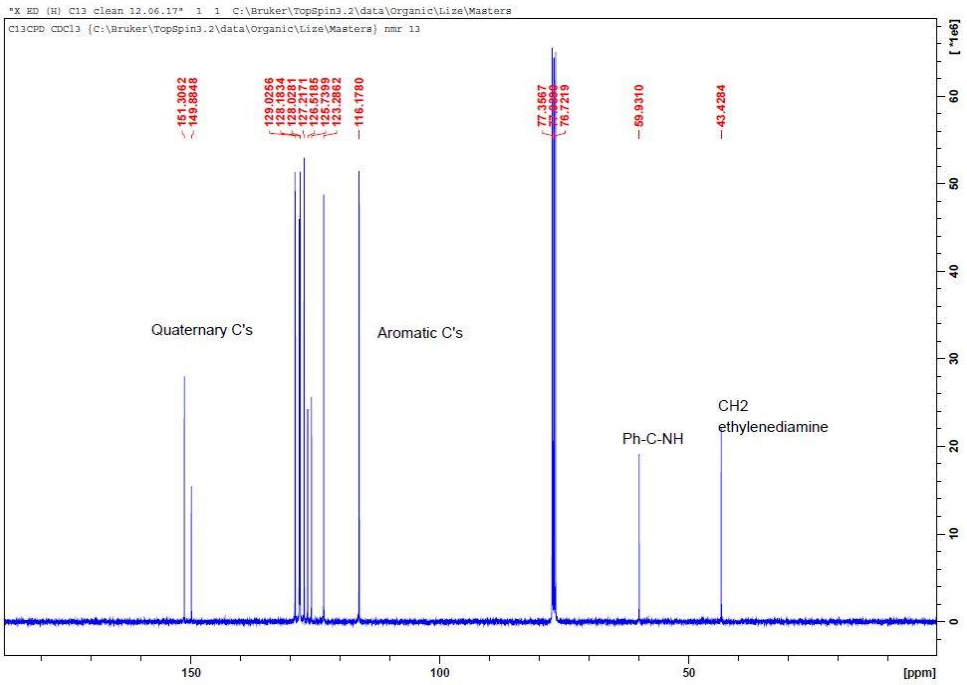


Figure S21e. ^{13}C-NMR spectrum for **H_2**.

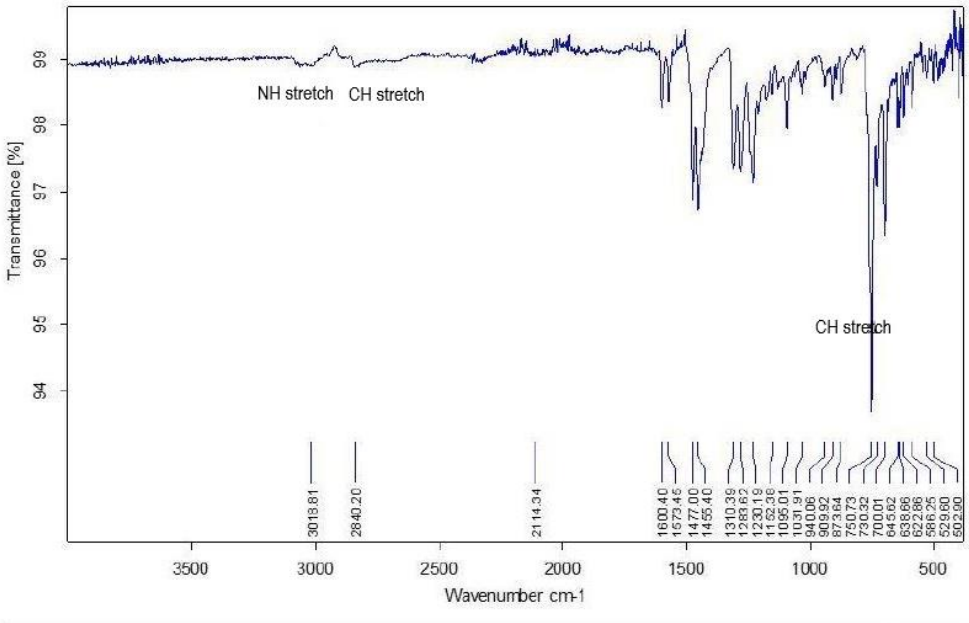


Figure S21f. IR spectrum for **H_2**.

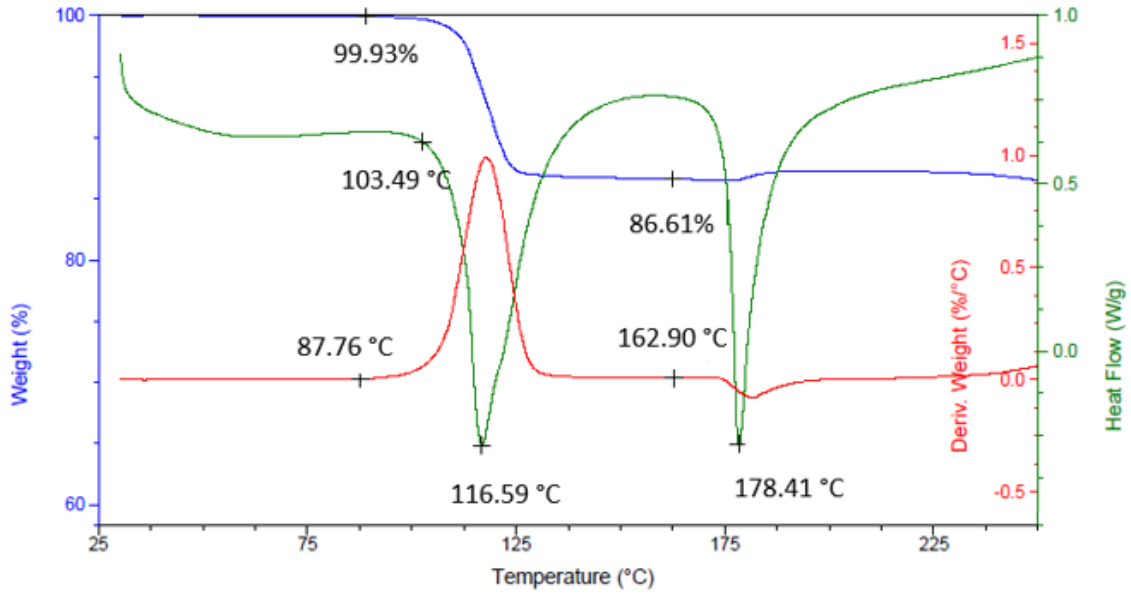


Figure S22a. Overlaid thermal traces (DSC, TG and DTG) for the **H_1**·ANI complex

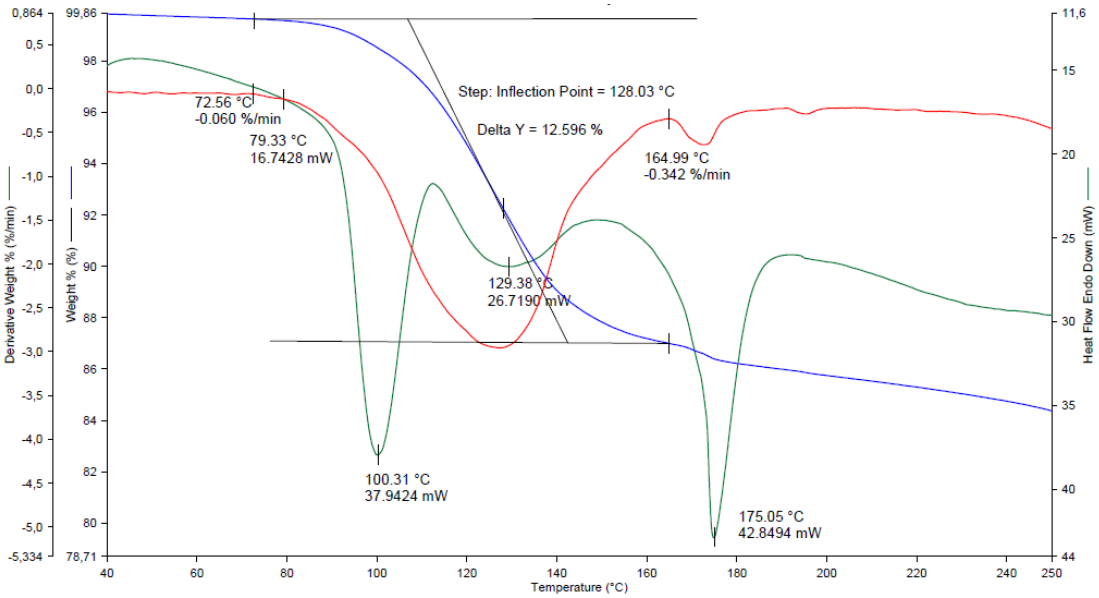


Figure S22b. Overlaid thermal traces (DSC, TG and DTG) for the **H_1**·NMA complex

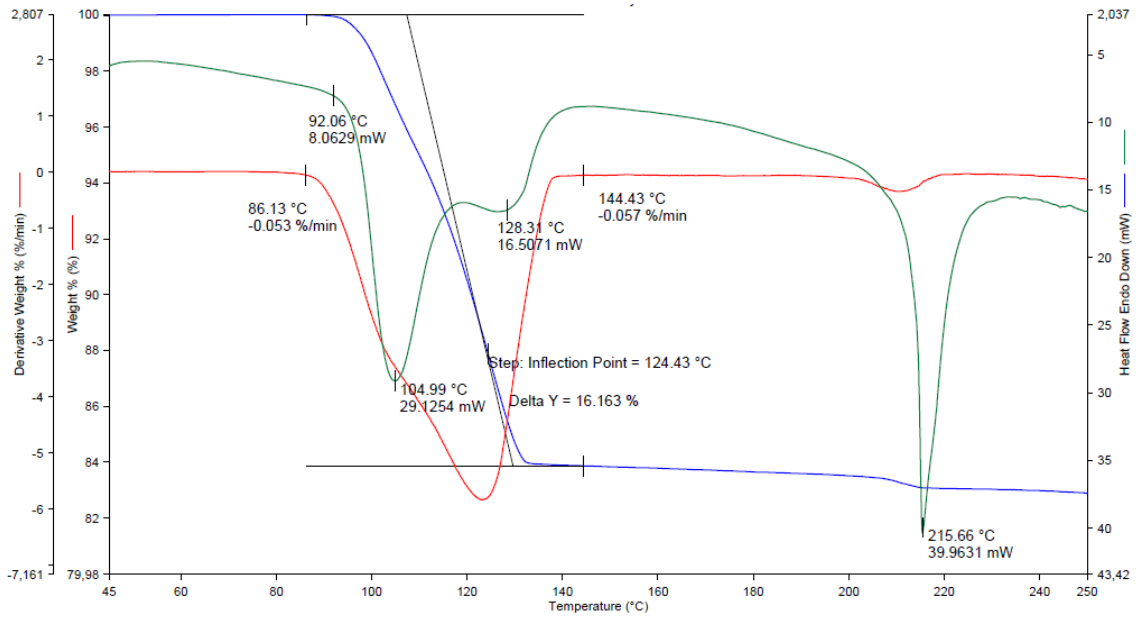


Figure S22c. Overlaid thermal traces (DSC, TG and DTG) for the **H_2**·NMA·0.406(H_2O) complex

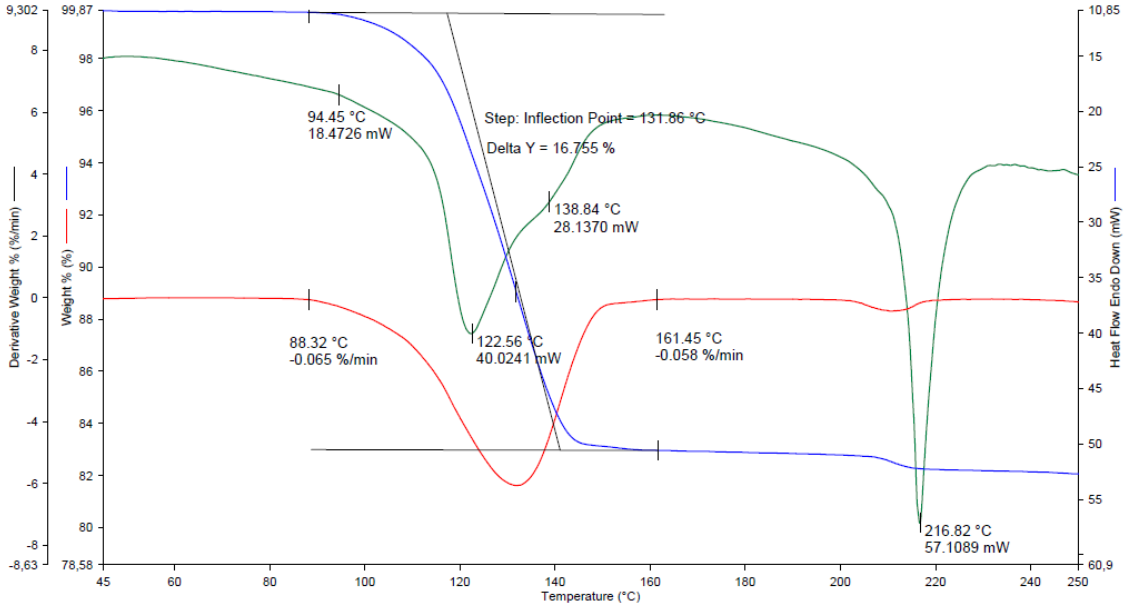


Figure S22d. Overlaid thermal traces (DSC, TG and DTG) for the **H_2**·NNDMA complex