SUPPORTING INFORMATION

Spin Crossover Metal-Organic Frameworks with Inserted Photoactive Guests: On the Quest to Control the Spin State by Photoisomerization

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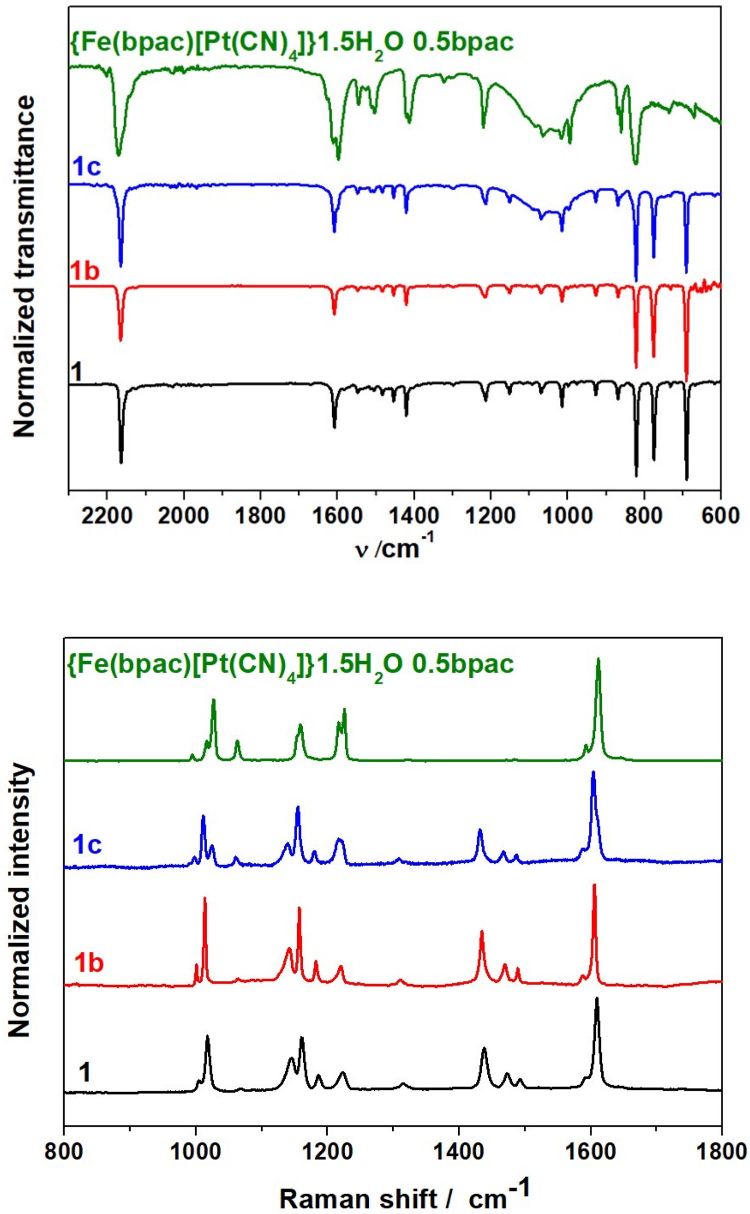
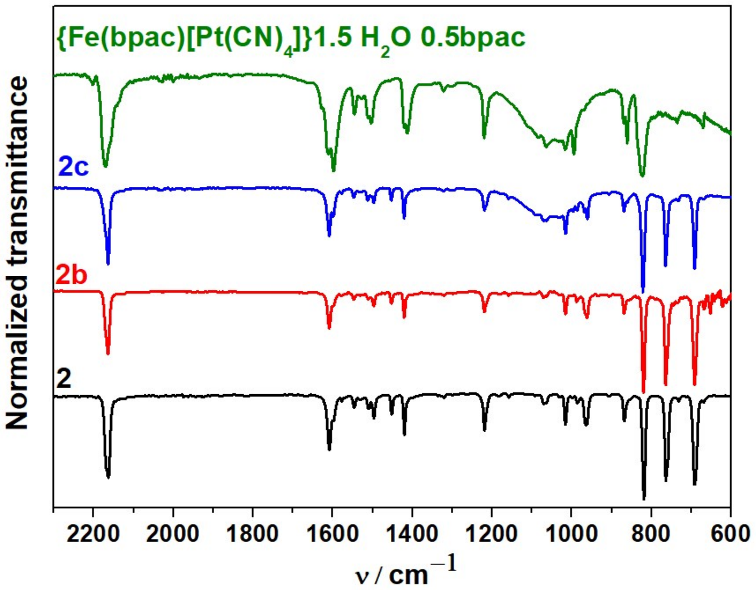
(a)


{Fe(bpac)[Pt(CN)4]}1.5H2O 0.5bpac
1c
1b
1
Normalized transmittance
2200 2000 1800 1600 1400 1200 1000 800 600
ν /cm-1
{Fe(bpac)[Pt(CN)4]}1.5H2O 0.5bpac
1c
1b
1
Normalized intensity
800 1000 1200 1400 1600 1800
Raman shift / cm-1

(b)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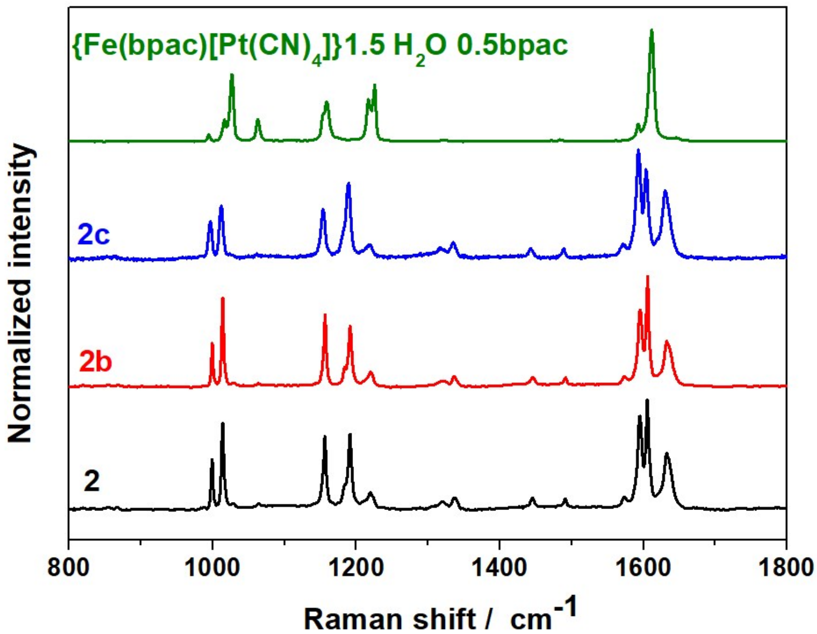
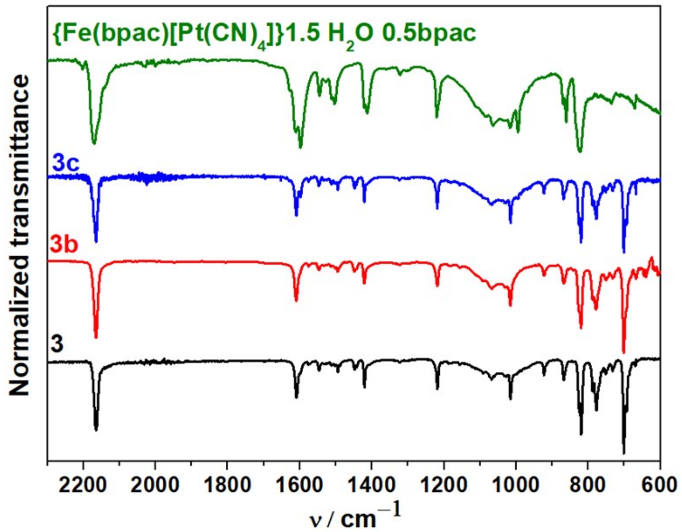
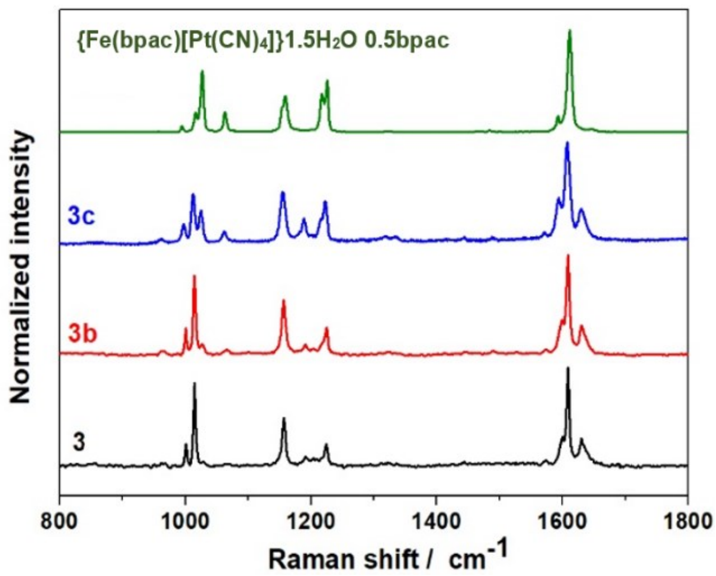
2c
2b
2
Normalized transmittance
2200 2000 1800 1600 1400 1200 1000 800 600
ν / cm−1


{Fe(bpac)[Pt(CN)4]}1.5 H2O 0.5bpac
2c
2b
2
Normalized intensity
800 1000 1200 1400 1600 1800
Raman shift / cm-1

(c)



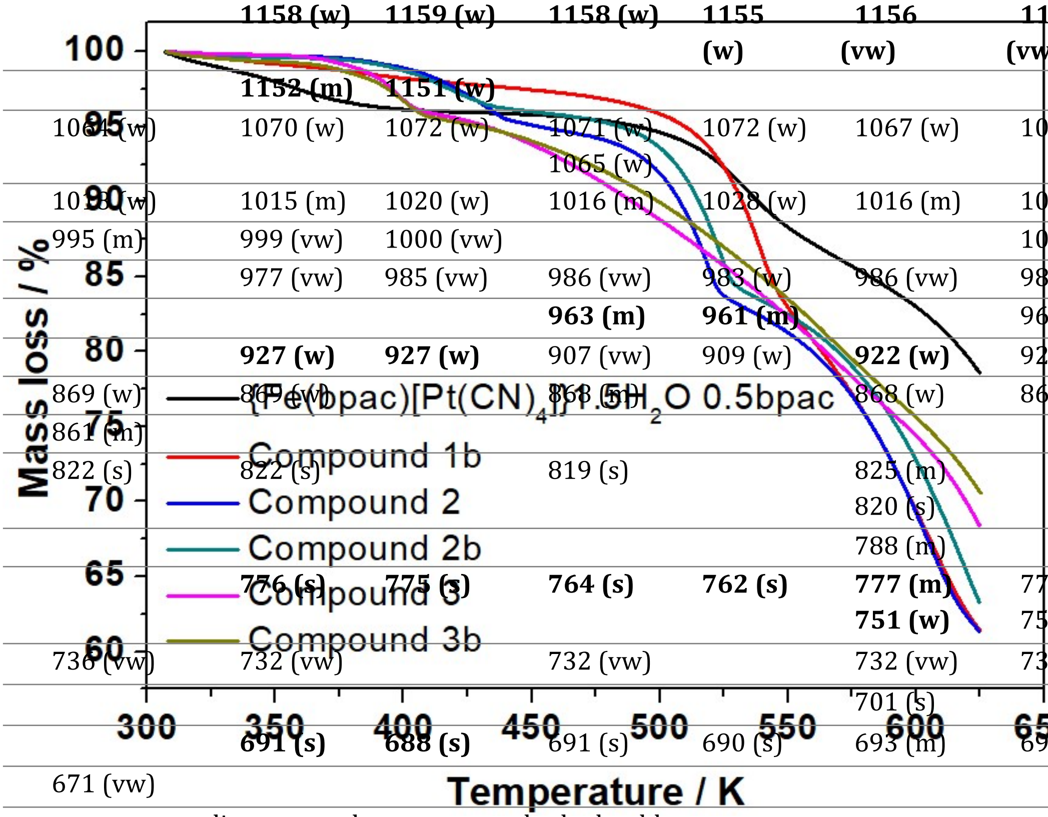


SI-1. Room temperature FTIR (up) and Raman (down) spectra (532 nm excitation) of the compounds **(a) 1-1c**, **(b) 2-2c** and **(c) 3-3c** compared to the spectra of $\{Fe(bpac)[Pt(CN)_4]\}\cdot 1.5H_2O\cdot 0.5bpac$.

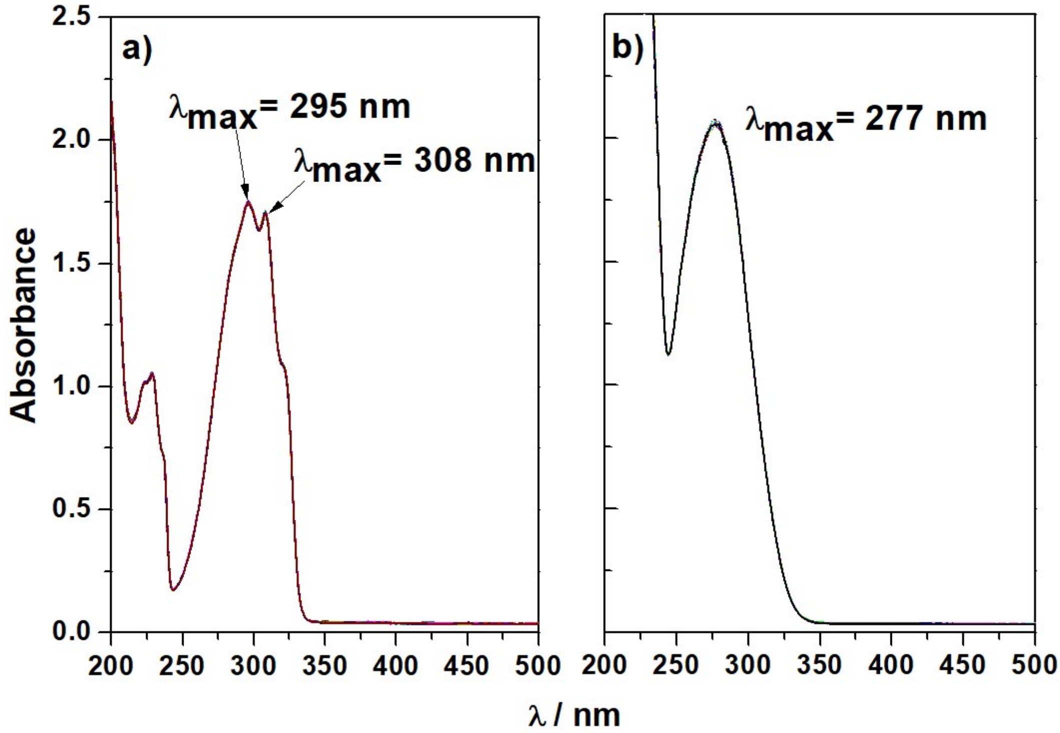
SI-3. Experimental IR vibrational wavenumbers of compounds **1-3** compared to the host material **$\{Fe(bpac)[Pt(CN)_4]\}\cdot 1.5H_2O\cdot 0.5bpac$** and the pure guest compounds.

host	1	*trans* azobenzene	2	*trans* stilbene	3	*cis* stilbene
Exp	**Exp**	**Exp**	**Exp**		**Exp**	**Exp**
2170 (s)	2165 (s)		2163 (s)		2165 (s)	
1611 (m)	1609 (m)		1609 (m)		1609 (m) 1600 (sh)	 1600 (m)
1598 (s)	 1584 (vw)	 1583 (vw)	1599 (sh) 1578 (vw)	1599 (w) 1577(vw)	 1576 (vw)	 1576 (w)
1545 (w)	1548 (w)		1546 (w)		1546 (w)	
1504 (w)	1506 (w)		1510 (w)		1512 (w)	
	1484 (w)	**1483 (w)**	**1497 (w)**	**1495 (w)**	**1495 (w)**	**1495 (m)** **1490 (m)**
	1453 (w)	**1453 (w)**	**1452 (w)**	**1451 (w)**	**1448 (w)** **1443 (w)**	**1448 (m)** **1443 (m)**
1421 (m)	1421 (m)		1420 (m)		1421 (m)	 1406 (w)
1413 (m)						
1322 (vw)	1299 (vw)	1300 (w)	1321 (vw)	1331 (w)		
1220 (m)		1222 (w)		1299 (w)		
1215 (sh)	1214 (m)		1219 (m)	1220 (w)	1218 (m)	 1180 (w)
	1158 (w)	**1159 (w)**	**1158 (w)**	**1155 (w)**	**1156 (vw)**	**1156 (vw)**
	1152 (m)	**1151 (w)**				
1064 (w)	1070 (w)	1072 (w)	1071 (w) 1065 (w)	1072 (w)	1067 (w)	1074 (m)
1018 (w)	1015 (m)	1020 (w)	1016 (m)	1028 (w)	1016 (m)	1028 (m)
995 (m)	999 (vw)	1000 (vw)				1000 (vw)
	977 (vw)	985 (vw)	986 (vw)	983 (vw)	986 (vw)	983 (vw)
			963 (m)	**961 (m)**		965 (vw)
	927 (w)	**927 (w)**	907 (vw)	909 (w)	**922 (w)**	923 (m)
869 (w)	869 (w)		868 (m)		868 (w)	862 (m)
861 (m)						
822 (s)	822 (s)		819 (s)		825 (m) 820 (s)	
					788 (m)	
	776 (s)	**775 (s)**	**764 (s)**	**762 (s)**	**777 (m)** **751 (w)**	778 (s) 751 (m)
736 (vw)	732 (vw)		732 (vw)		732 (vw)	732 (w)
					701 (s)	
	691 (s)	**688 (s)**	691 (s)	690 (s)	693 (m)	693 (s)
671 (vw)						

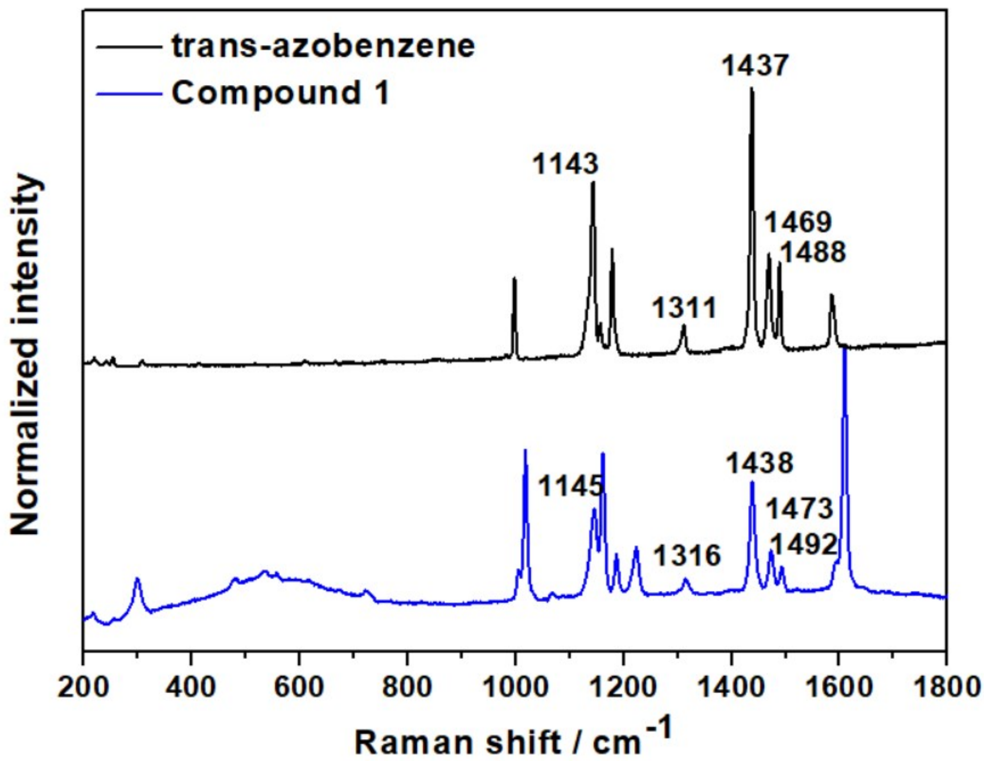
s – strong, m-medium, w-weak, vw-very weak, sh-shoulder

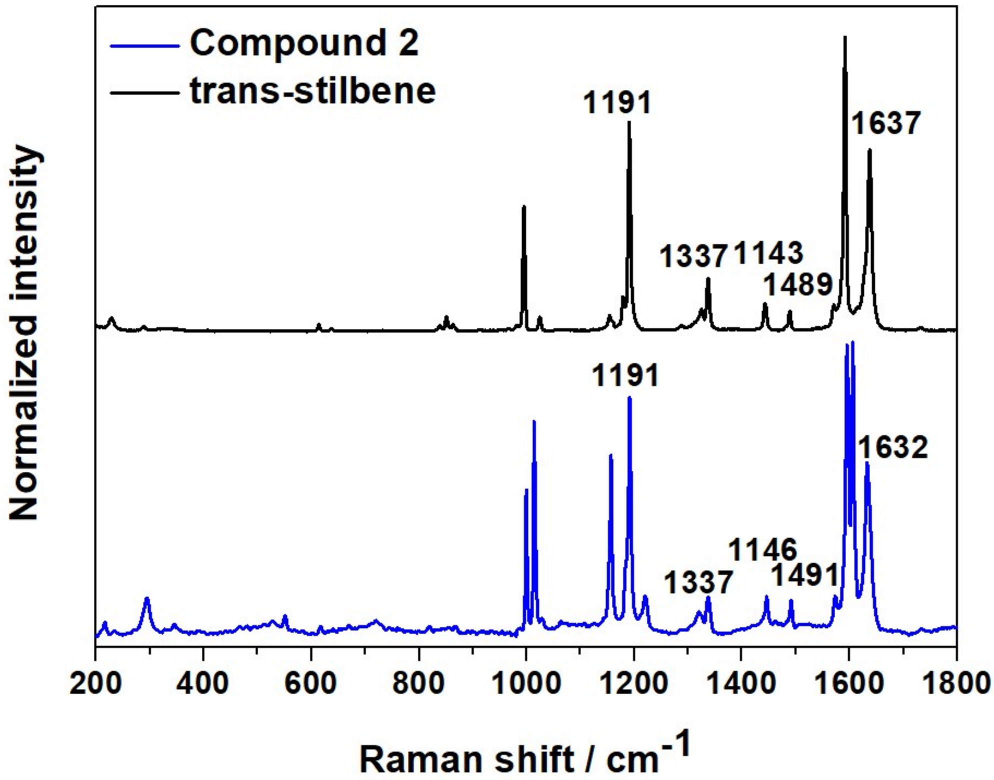


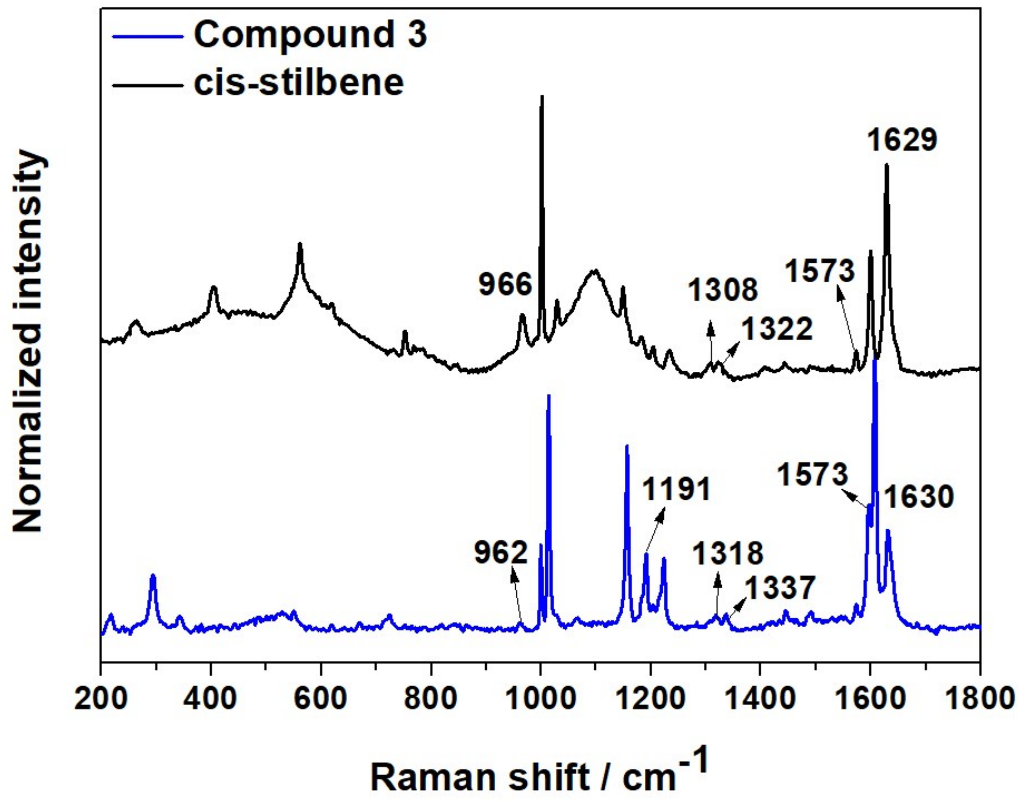
SI-2. Thermogravimetric curves of the powder samples.



SI-4. UV-VIS absorption spectra collected every minute over 2 hours of a water-ethanol solution of **(a)** *trans*-stilbene and **(b)** *cis*-stilbene under ambient light.





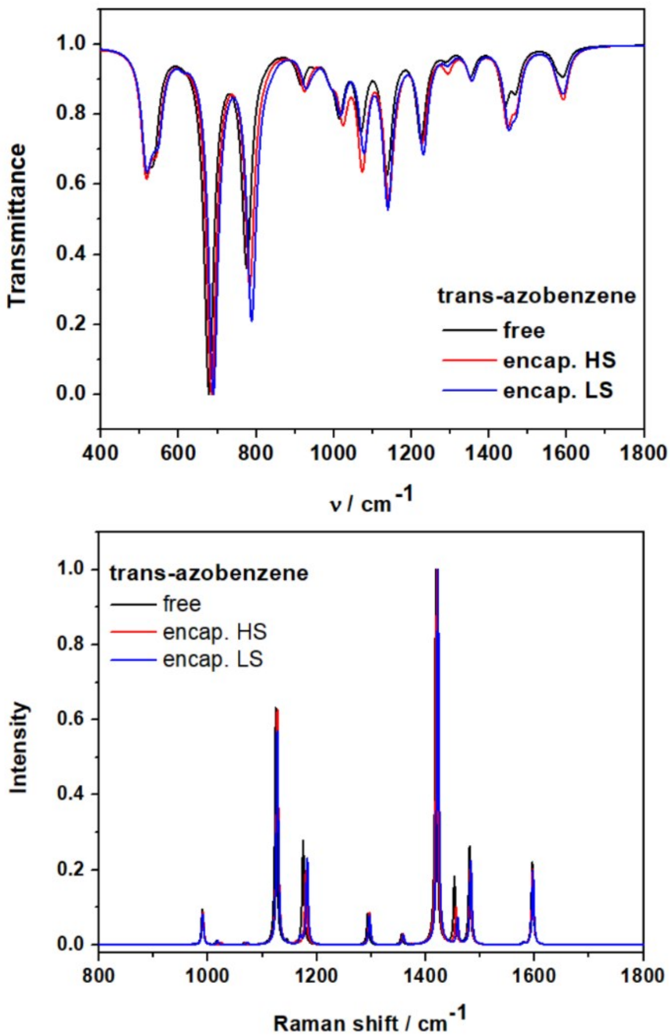


SI-5. Raman spectral fingerprints (532 nm excitation) of guest molecules in compounds **1**-**3.**

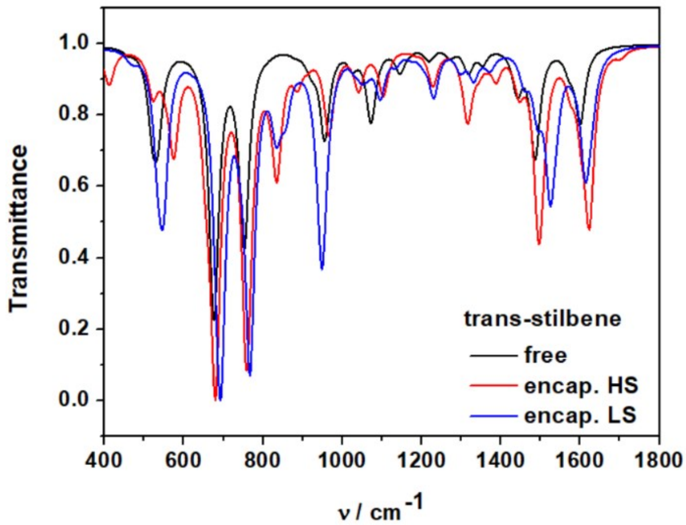
SI-6. Well-distinguishable peaks present in the room-temperature Raman of host {Fe(bpac)[Pt(CN)$_4$]}·1.5H_2O·0.5bpac and compounds **1-3** measured by different laser sources.

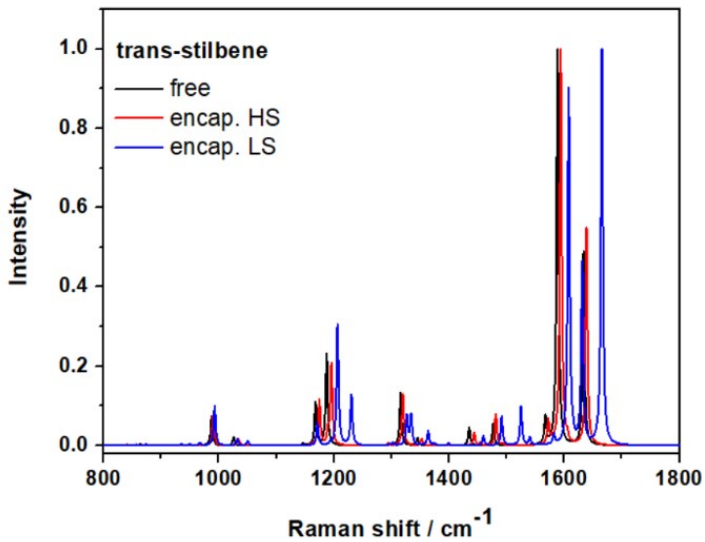
host material		**1**		**2**			**3**		
532	**785**	**355**	**532**	**355**	**532**	**785**	**355**	**532**	**785**
				1633	1632	1632	1631	1630	1628
1612	1611	1606	1609	1596	1606	1604		1607	1607
1592	1592	1592	1594		1595	1593	1596	1597	1597
		1587		1573	1573	1574	1573	1573	1571
1483	1484	1489	1492	1491	1491	1490	1491	1491	1494
		1468	1473	1445	1446	1445	1447/5	1445	1441
		1433	1438	1336	1337	1336	1336	1337	
			1316	1317	1314	1320	1317	1318	1320
		1308		1300			1300		1304
1226	1224		1223		1220	1219		1223	1223
1217	1217							1203	1203
		1182	1186	1189	1191	1190	1189	1191	1189
				1184			1182		
1159	1159		1162	1156	1157	1155	1153	1156	1156
1154	1154	1142	1145						
1062	1064		1068		1063			1066	1068
1027	1028				1029	1029			1030
1016	1017		1017		1014	1014		1014	1014
994	995	999	1004	997	999	999	997	1000	1000
		985						959	961
						868			867
						855			
						819			818
									770
730	733	755	721			727	755	724	752
									727
	670				671	670		669	668
				640		640	643		
				615	617	617	615	618	619
559	553		557		551	550		551	550
			533						
	381		480			468			406
320	326					341		342	343
		274	299	286	294	294		293	294
		222							263
			216	208	216	219	206	217	218

(a)

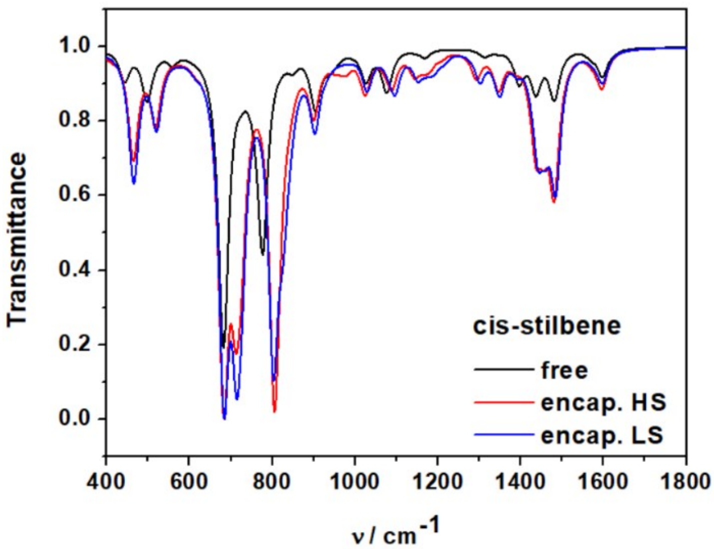

Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
1200
1400
1600
1800
ν / cm-1
trans-azobenzene
free
encap. HS
encap. LS
Intensity
1.0
0.8
0.6
0.4
0.2
0.0
800
1000
1200
1400
1600
1800
Raman shift / cm-1
trans-azobenzene
free
encap. HS
encap. LS

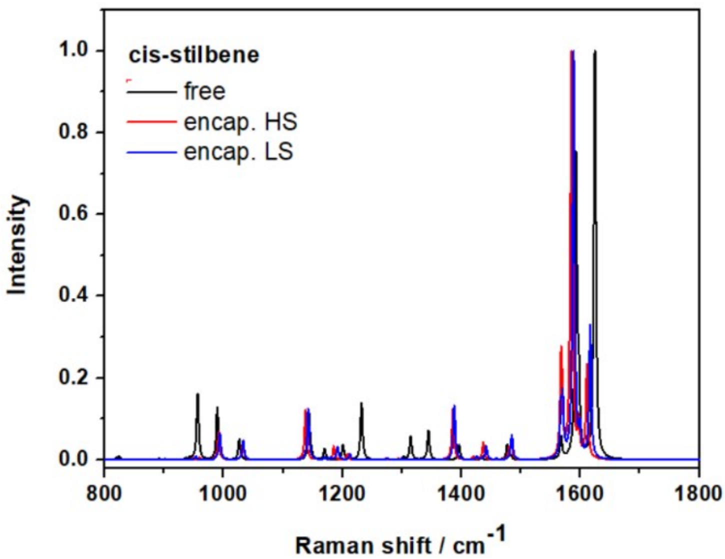
(b)


Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
1200
1400
1600
1800
ν / cm-1
trans-stilbene
free
encap. HS
encap. LS

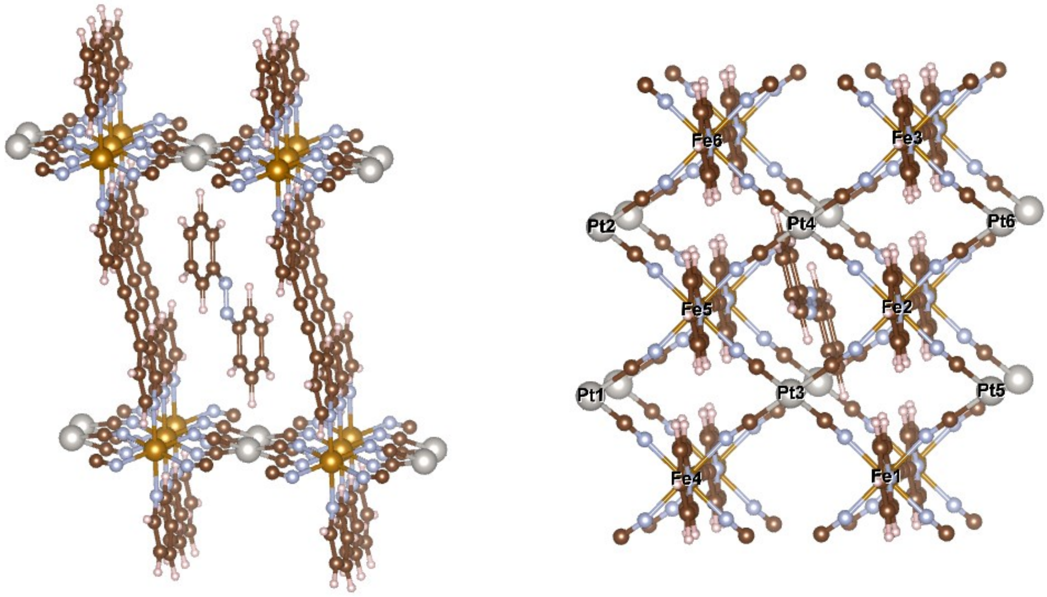


(c)





SI-7. Calculated FTIR (up) and Raman (down) spectra of free and encapsulated **(a)** *trans*-azobenzene, **(b)** *trans*-stilbene and **(c)** *cis*-stilbene.



SI-8. The model of cavity and encapsulated molecule as it was used in the QM/MM calculations. Shown is the case of MOF in HS state with *trans*-azobenzene, view perpendicular on the guest molecule (left) and parallel with the guest molecule with displayed also labels of atoms (right).

SI-9. Values of calculated CHELPG charges on metallic centers of the model cavity. The labelling of atoms is shown in Fig. SI-8.

	LS state	**HS state**
Pt1	0.56	0.46
Pt2	0.55	0.46
Pt3	0.12	-0.21
Pt4	0.11	-0.21
Pt5	0.55	0.44
Pt6	0.55	0.44
Fe1	-2.32	-0.21
Fe2	-2.15	0.11
Fe3	-2.20	-0.14
Fe4	-2.22	-0.17
Fe5	-2.27	-0.06
Fe6	-2.45	-0.22

SI-10. FTIR peaks of guest molecules before and after encapsulation. The calculated data are compared with the experiment (at 293 K).

***trans*-azobenzene**					***trans*-stilbene**					***cis*-stilbene**				
calculated			experimental		calculated			experimental		calculated			experimental	
free	encap HS	encap LS	free	encap HS	free	encap HS	encap LS	free	encap HS	free	encap HS	encap LS	free	encap HS
					1600	1623	1616							
1590	1591	1591	1583	1584			1525	1597	1598	1597	1595	1597	1600	1600
								1577	1578				1576	1576
1466	1466	1466	1483	1483	1487	1496	1495	1495	1497	1480	1479	1482	1495	1495
													1490	1489
1440	1448	1451	1453	1454	1441	1447	1461	1451	1452	1437	1439	1445	1448	1448
1352													1443	1443
1334	1355	1356			1351	1387	1371			1397			1406	
					1318	1316	1331	1331			1347	1349		
1288	1294	1292	1300	1299			1298	1300			1293	1301	1203	1204
1224	1228	1230	1222	1214	1217	1228	1230	1219	1219				1180	
						1187		1182	1182					
			1159	1158	1146	1178		1155	1158	1168	1145	1152	1156	1156
1137	1141	1139	1151	1151		1103		1105					1106	
1070	1073	1077	1072	1070	1075		1094	1072	1071	1075	1086	1094	1074	
						1041	1051							
1014	1023	1017	1020		1027			1028	1031	1026	1025	1029	1028	
1022			1000	999				983	986				1001	986
	993(sh)	992(sh)	985	987	956	966	949	961	964				982	
915	924	931	927	927		886							965	923
								909	907				923	
						832	836	847		905	900	904		
775	783	788	775	776		759							862	
													844	
					752		767	762	764		805	804		777
678	684	689	688	691						777			778	752
					676	680	692						751	732
													732	
532(sh)	539 (sh)	545(sh)						690	691	713	713	715		694
517	517	519				575				682	684	684	692	
					528	525	544	540	535					

SI 11. Raman peaks of guest molecules before and after encapsulation. The calculated data are compared with the experiment.

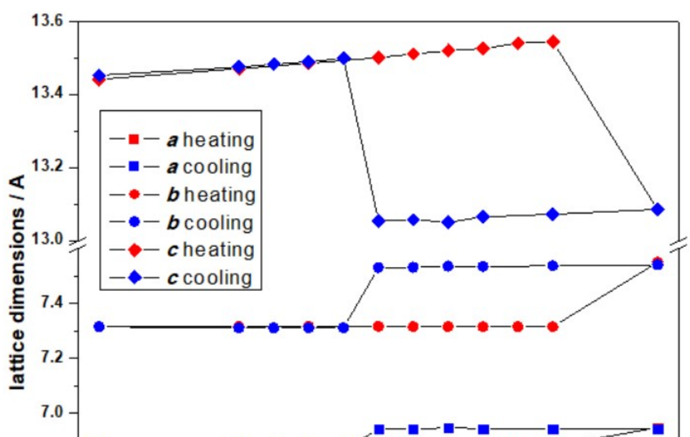
***trans*-azobenzene**						***trans*-stilbene**						***cis*-stilbene**					
calculated			experimental			calculated			experimental			calculated			experimental		
free	encap HS	encap LS	free	encap HS	encap LS	free	encap HS	encap LS	free	encap HS	encap LS	free	encap HS	encap LS	free	encap HS	encap LS
						1634	1638	1665	1637	1632	1635	1624	1611	1616	1629	1630	1632
								1631	1591	1595	1598	1593	1597	1599	1599	1597	
1596	1596	1597	1585			1588	1594	1608	1571	1573	1576	1586	1585	1589	1573	1573	
				1487	1495	1567	1572	1582					1568	1570	1491	1491	
				1467	1474			1540				1477	1483	1485	1444	1445	
1481	1482	1483	1489	1432	1438			1525				1434	1437	1441			
1453	1455	1459	1469	1310	1316	1477	1481	1491	1489	1491	1492	1396	1385	1424			
1355	1420		1438			1435	1443	1459	1443	1446		1334		1388	1321	1337	
	1358	1359	1311									1315			1308		
1293	1297	1297				1345	1352	1364	1337	1337	1339	1232			1234	1223	1223
						1316	1320	1334	1325	1320		1201	1208	1213	1204	1203	
		1182		1180	1189			1327				1170	1185	1192		1191	1196
1175	1179	1170	1179					1302	1289								
			1157					1230				1143	1138	1142	1149	1156	1158
1145			1143	1139	1149	1187	1195	1206	1191	1191	1193				1100		
	1128	1128				1168	1175	1171	1179			1026	1032	1033	1029		
1124								1050	1154								
						1025	1033	1032	1024			989	991	994	1001	1000	
		1072	998			987	990	993	995	999	999	956	959	953	966	959	
1066		1018						967	981				947				
1015	991	990						949				891		901			
989						863	865	874	863			850	845	845			
914	663		608			839	841	857	851			824					
663	606	605							839								
605												777	774	774			
												763			752		
						638	636	643	638			745	737	738			
						611	613	614	614			724					
												612	618	618	619		

SI-12. Selected crystallographic information for crystal structures of compound **1.**

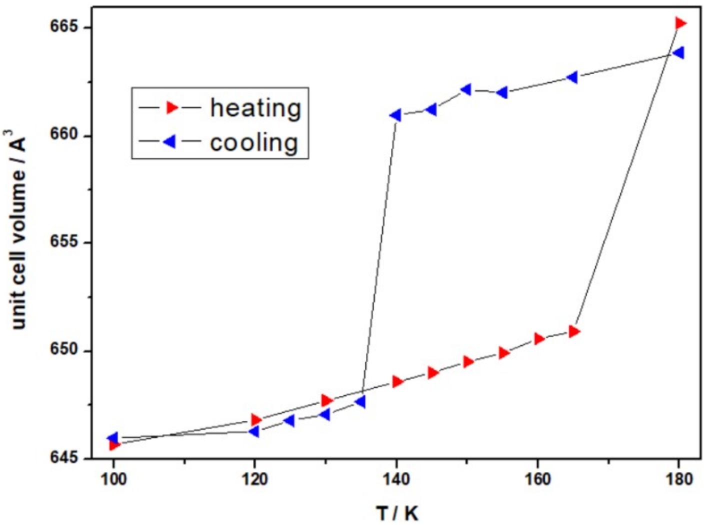
	1@100 K	1@180 K
Formula	$C_{28}H_{18}FeN_8Pt$	$C_{28}H_{18}FeN_8Pt$
M_w/ g mol^{-1}	717.44	717.44
Crystal colour	red	red
Temperature / K	100(1)	180(1)
Wavelength / Å	1.54186	1.54186
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a / Å	6.8681(2)	6.9483(3)
b / Å	7.3161(2)	7.5509(3)
c / Å	13.4430(5)	13.0859(5)
α /°	79.253(3)	77.715(3)
β /°	76.780(3)	82.604(3)
γ /°	89.413(3)	88.873(3)
V / Å^3	645.67(4)	665.24(5)
Z; ρ_{calc} / g.cm^{-3}	1, 1.222	1, 1.222
μ (Cu-K$_\alpha$)/mm^{-1}	14.762	14.328
F(000)	346	346
Crystal size / mm	0.18x0.13x0.05	0.12x0.08x0.06
θ range for the data collection / °	2.92 to 69.76	3.485 to 71.795
Final *R* indices [$I > 2\sigma(I)$]^a	R_1= 0.0493 wR_2 =0.1252	R_1= 0.0745 wR_2 =0.1940
R indices (all data)^a	R_1= 0.0494 wR_2= 0.1255	R_1= 0.0750 wR_2 =0.1958
GoF on F^2	1.069	1.070
CCDC number	2042716	2042717

$^a R1 = \sum(F_0 - F_C)/\sum(F_0)$; $wR2 = \sqrt{\sum[w(F_0^2 - F_C^2)^2]/\sum[w(F_0^2)^2]}$

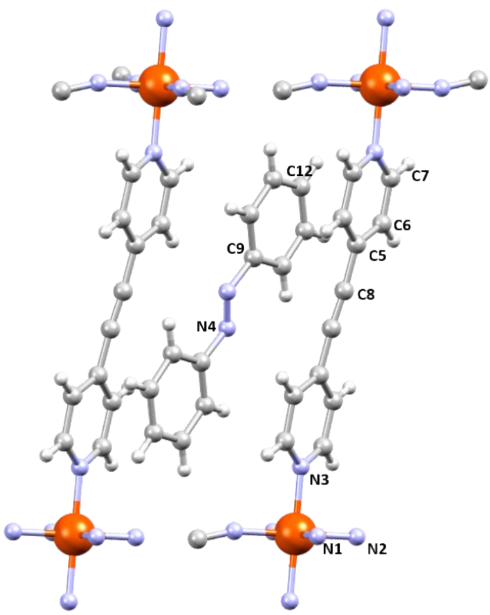
(a)



(b)

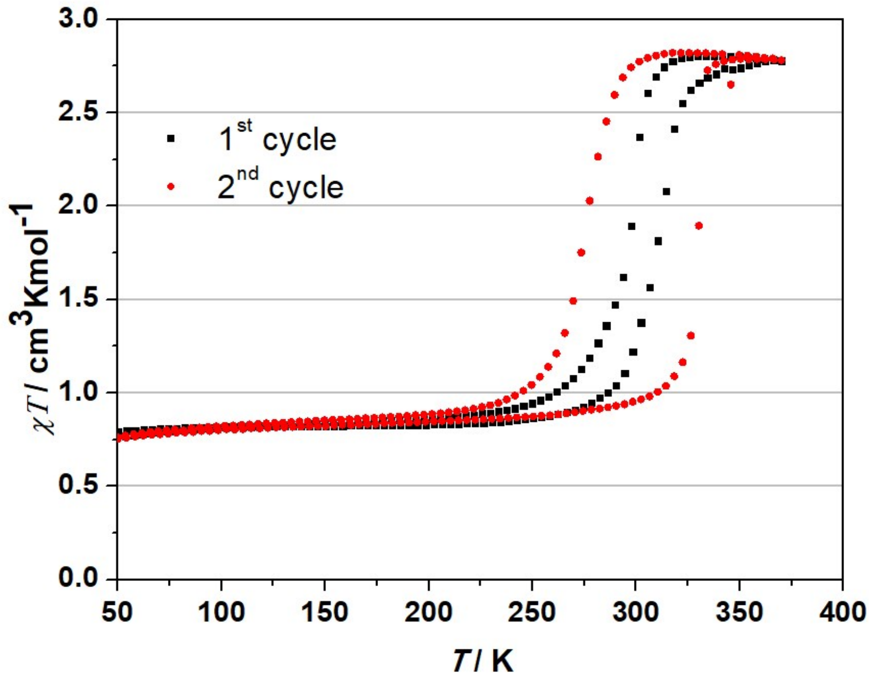


SI-13. Temperature evolution of **(a)** unit cell constants and **(b)** unit cell volume in the crystal structure of compound **1**.

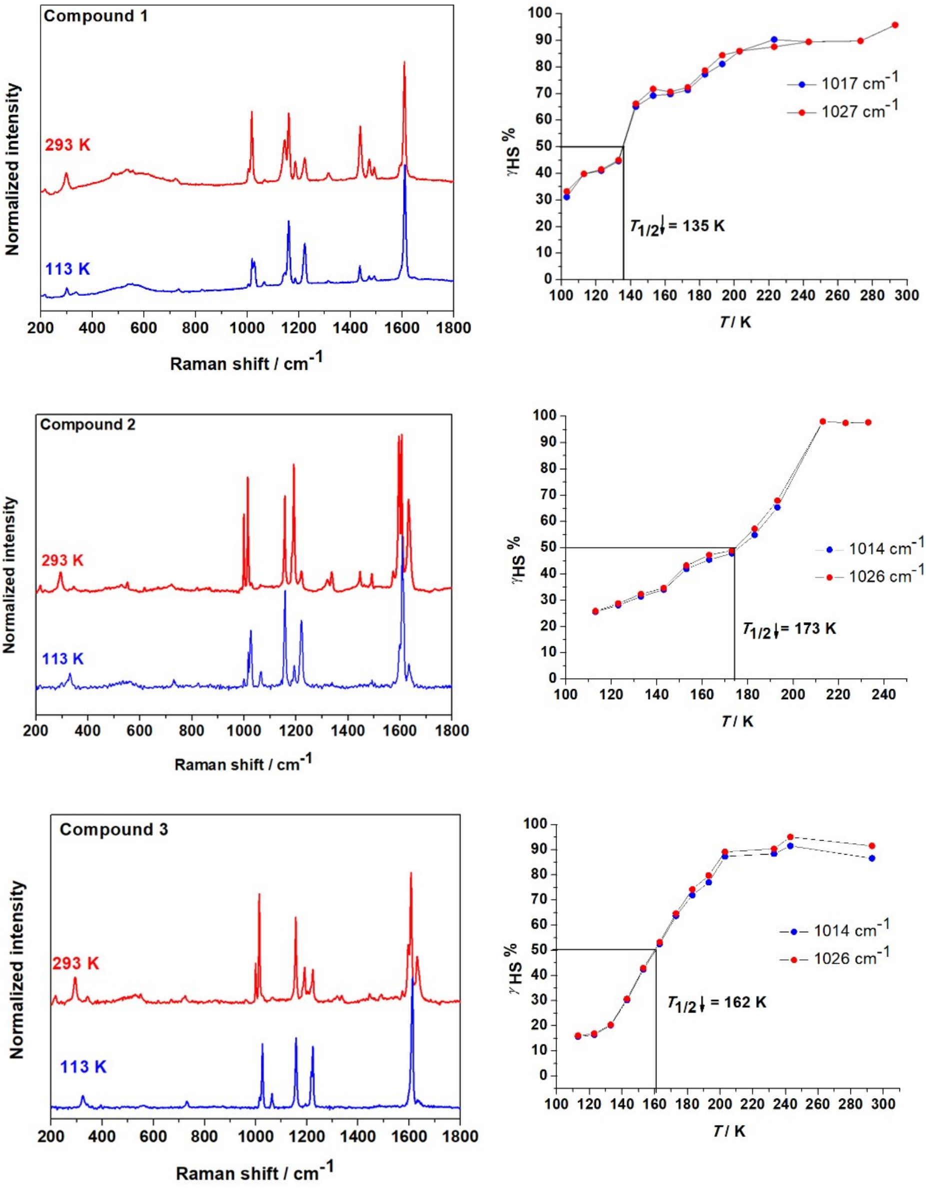


SI-14. Fe-N distances and non-covalent contacts between the **bpac** bridging ligands and guest *trans*-azobenzene molecule in the crystal structure **1** at

100 K: Fe-N1 = 1.926(6) Å, Fe-N2 = 1.926(6) Å, Fe-N3 2.008(5) Å, N4···C8= 3.630(11) Å, C9···C5= 3.694(11) Å, C9···C6= 3.635(11) Å, C12···C7= 3.525(11) Å; and at 180 K: Fe-N1= 2.137(8) Å, Fe-N2= 2.153(8) Å, Fe-N3= 2.217(9) Å, N4···C8 = 3.740(11) Å, C9···C5 = 3.806(11) Å, C9···C6 = 3.552(11) Å, C12···C7 = 3.606(11) Å.

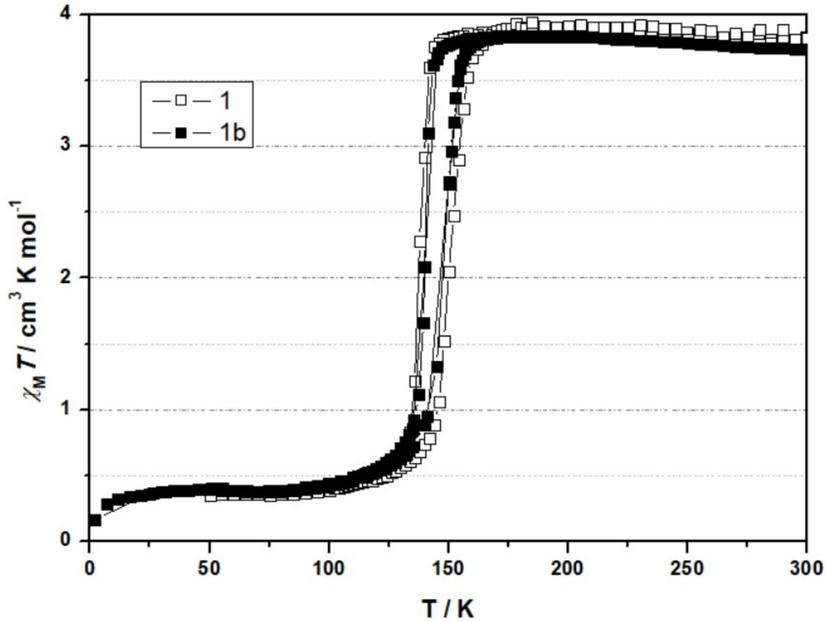


SI-15. Magnetic properties of the host system {Fe(bpac)[Pt(CN)$_4$]}·1.5H_2O·0.5bpac.

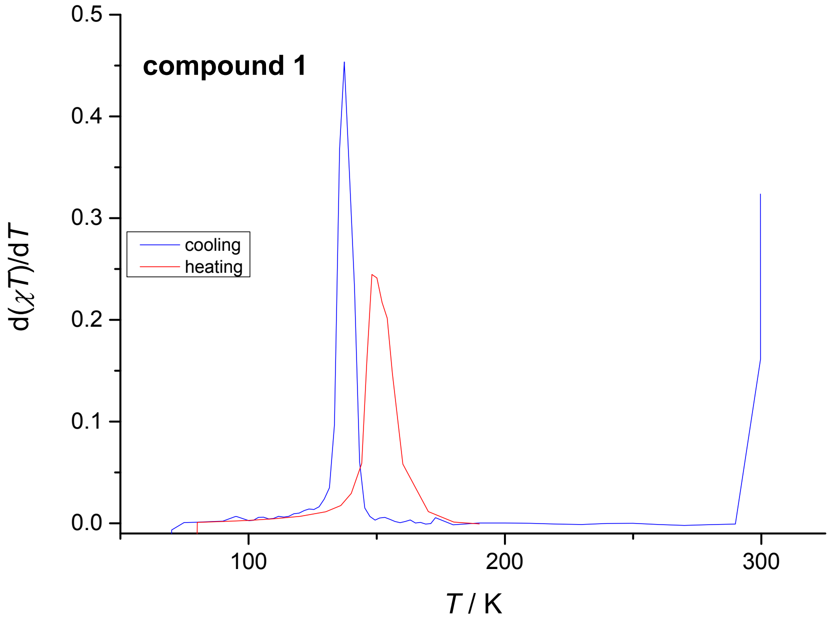


SI-16. Left: 532 nm Raman spectra of **1-3** recorded at 293 K (HS) and 113 K (LS). **Right:** Temperature dependent HS fraction (γ_{HS}) of **1-3** obtained by integration of Raman peak areas in the cooling mode. Data were collected every 10 K between 113 and 293 K.

(a

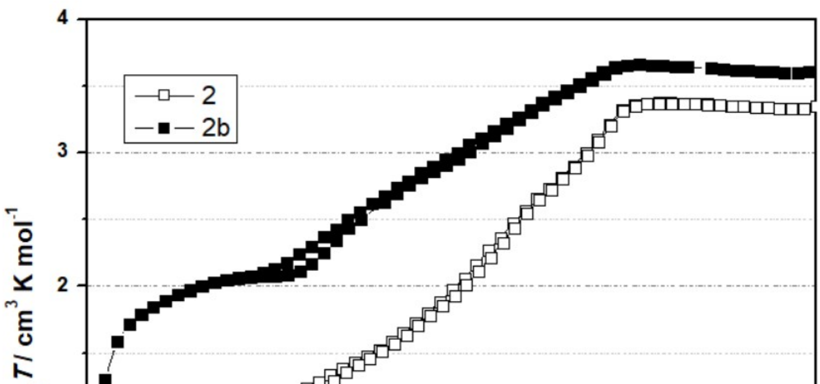


χMT / cm3 K mol-1
T / K
0
1
2
3
4
0
50
100
150
200
250
300
1
1b



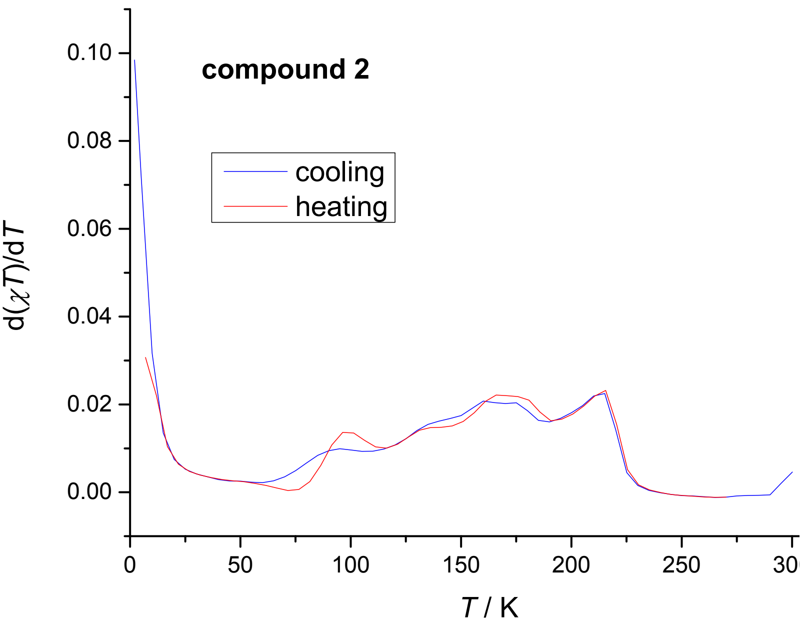
compound 1
d(χT)/dT
T / K
0.0
0.1
0.2
0.3
0.4
0.5
100
200
300
cooling
heating

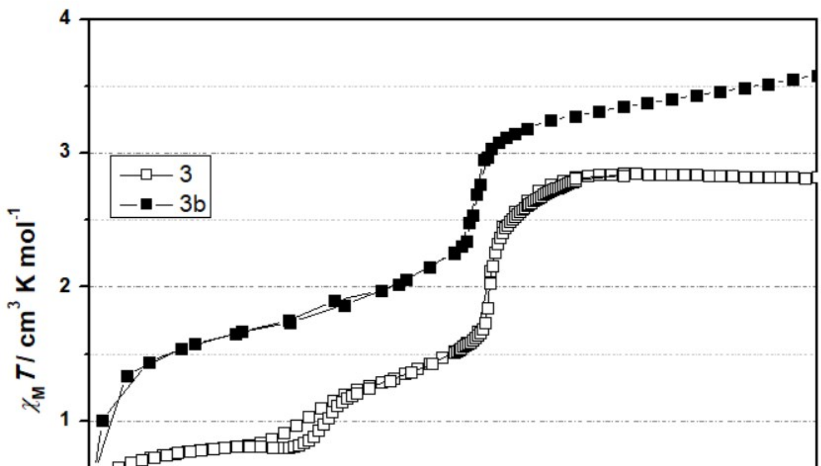
(b)



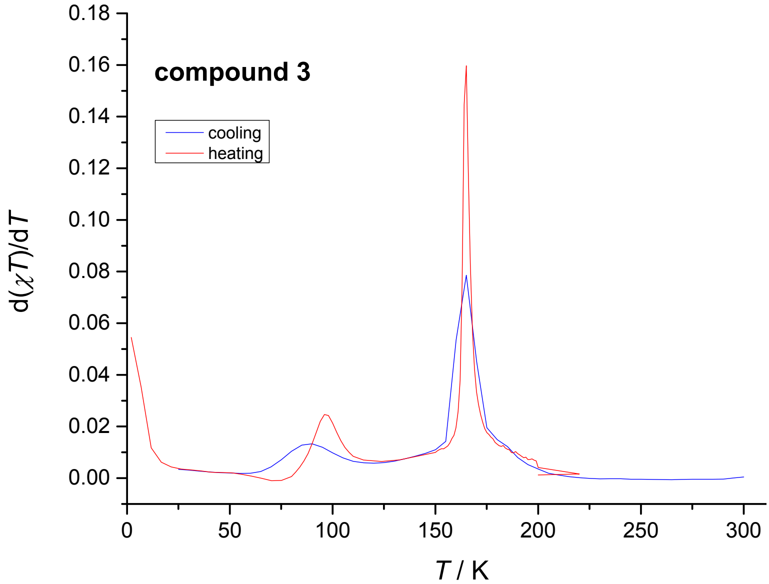
T / cm3 K mol-1
2
3
4
2
2b

8


compound 2
cooling
heating
d(χT)/dT
0.10
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
250
T / K

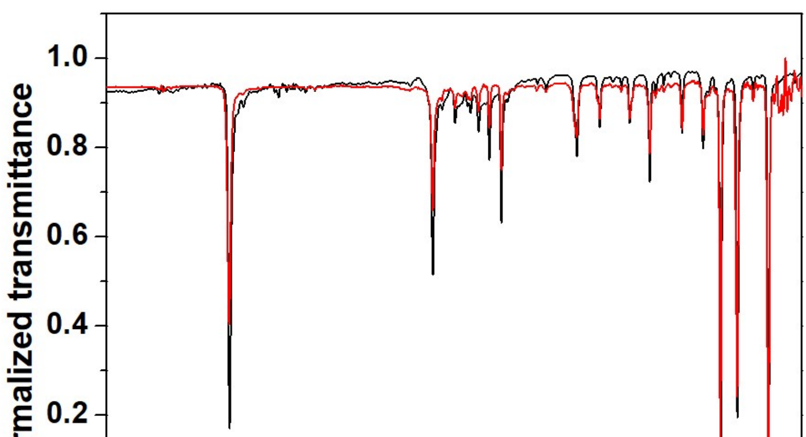

4
3
2
1
3
3b
χMT / cm3 K mol-1

9



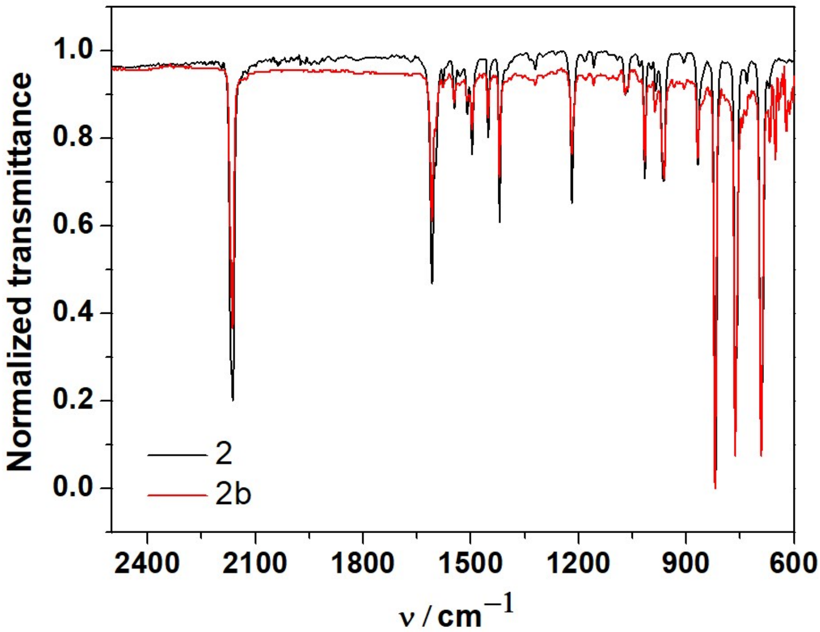
SI-17. Comparison of magnetic measurements on **(a) 1** and **1b, (b) 2** and **2b, (c) 3** and **3b.**

(a)

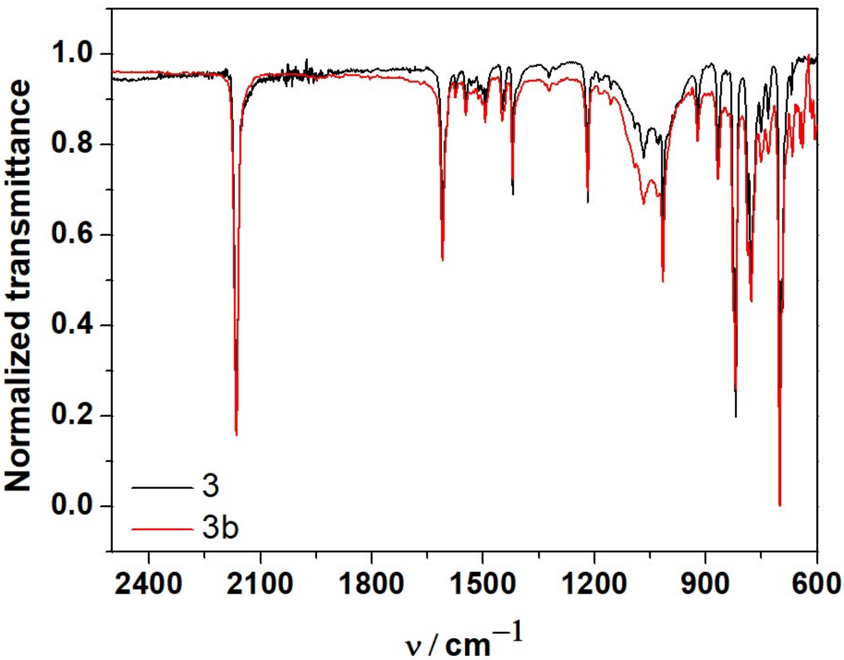


0

(b)

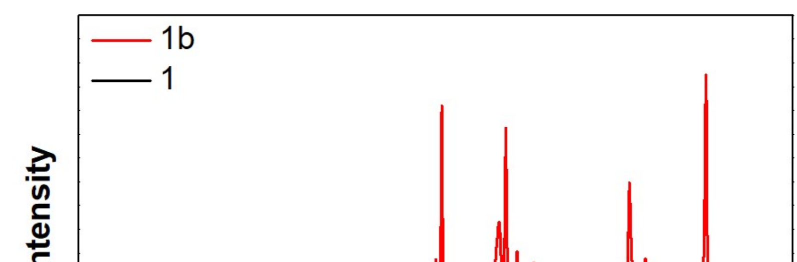


(c)



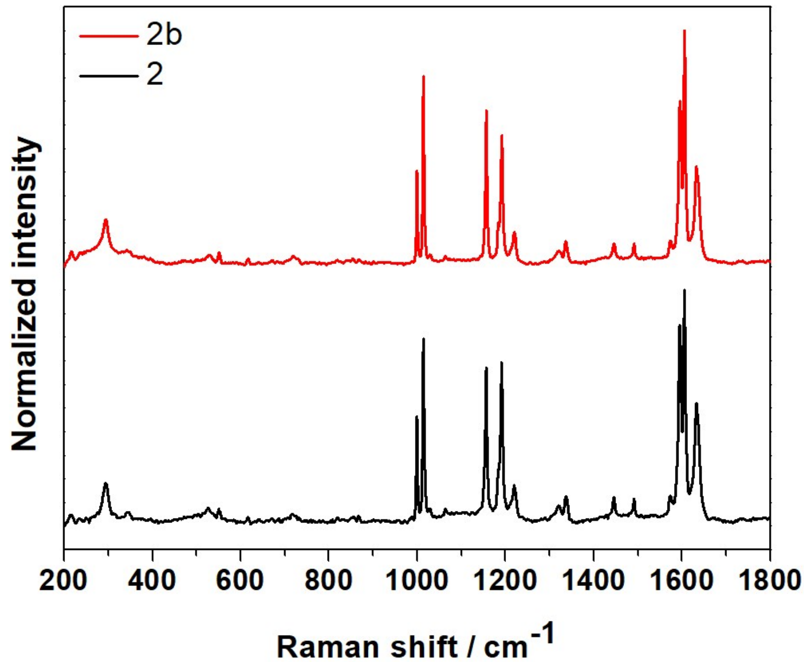
SI-18. FTIR spectra of **(a) 1** vs. **1b, (b) 2** vs. **2b** and **(c) 3** vs. **3b.**

(a)

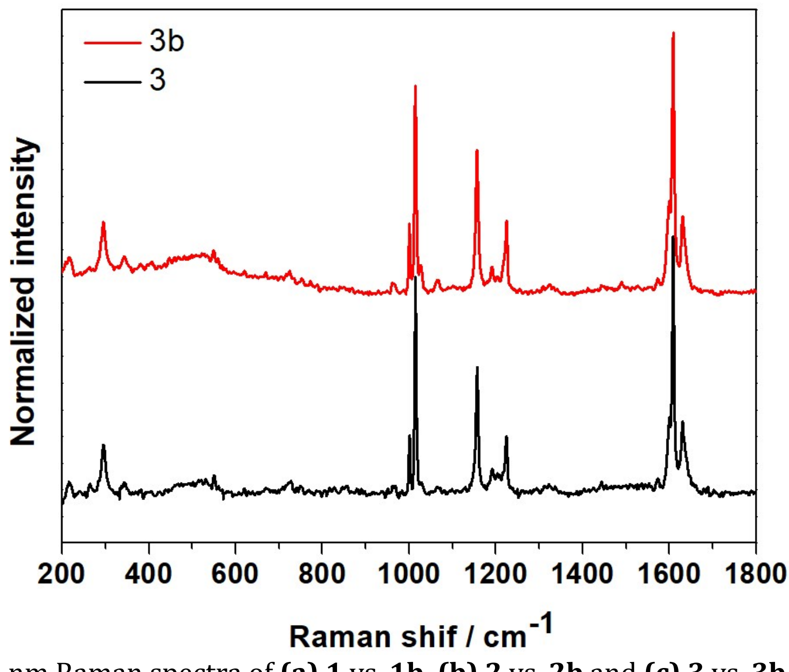


1

(b)

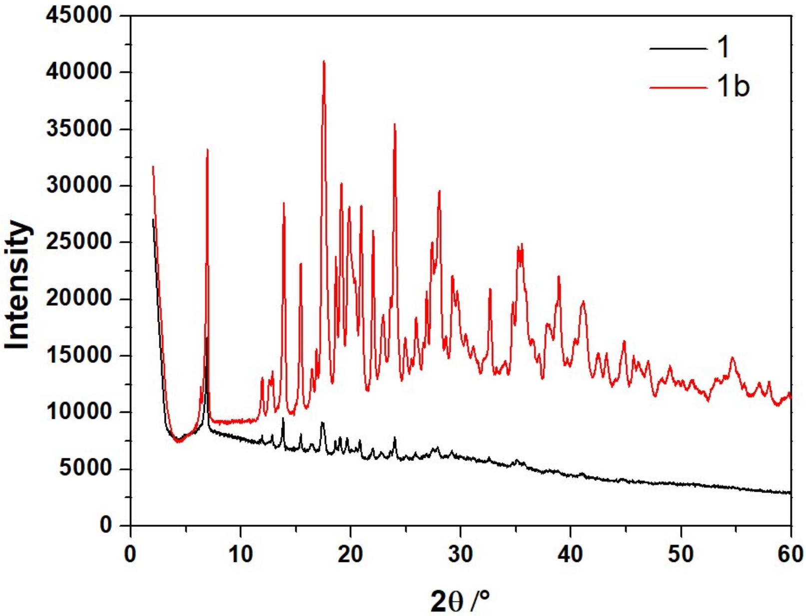


(c)

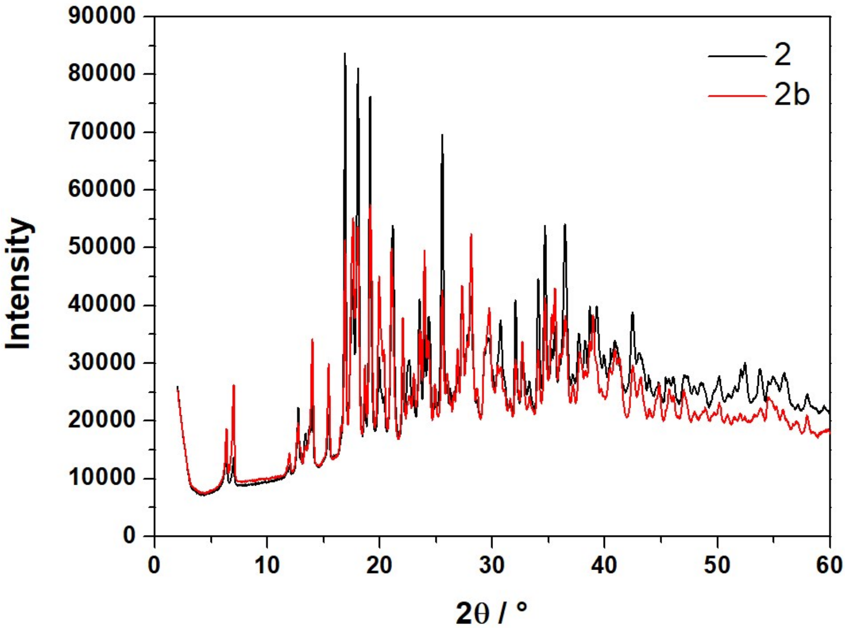


SI-19. 532 nm Raman spectra of **(a) 1** vs. **1b, (b) 2** vs. **2b** and **(c) 3** vs. **3b** at 293 K.

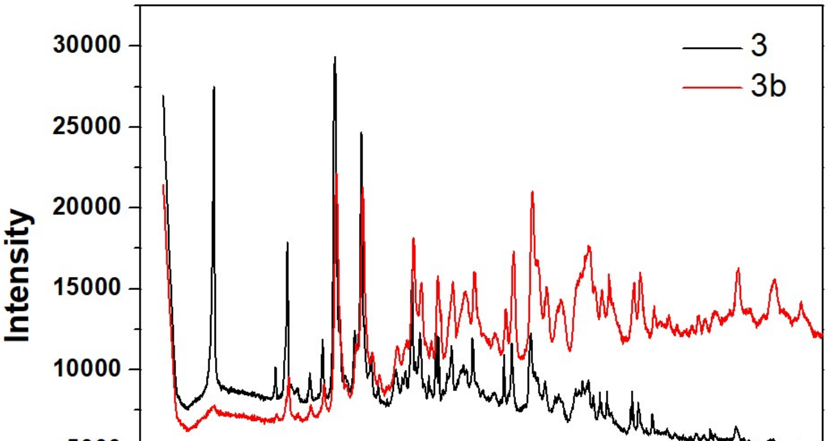
(a)


Intensity
2θ /°
1
1b
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
0
10
20
30
40
50
60

(b)

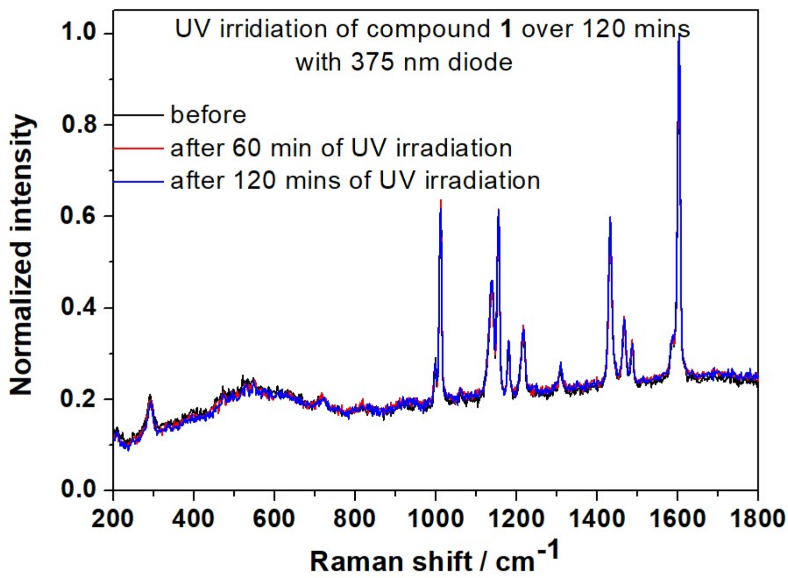

Intensity
2θ / °
2
2b
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
0
10
20
30
40
50
60

(c)

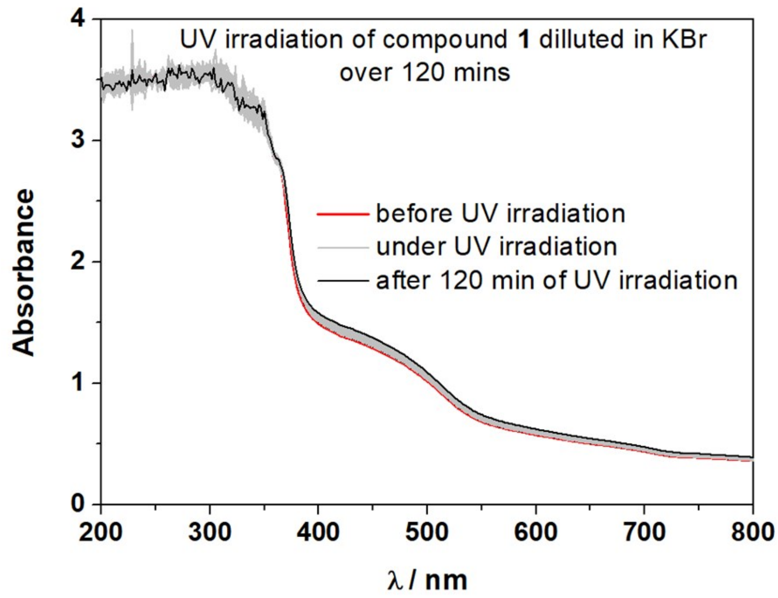

Intensity
3
3b
10000
15000
20000
25000
30000

SI-20. Powder X-ray diffractograms of **(a) 1** vs. **1b, (b) 2** vs. **2b** and **(c) 3** vs. **3b.**

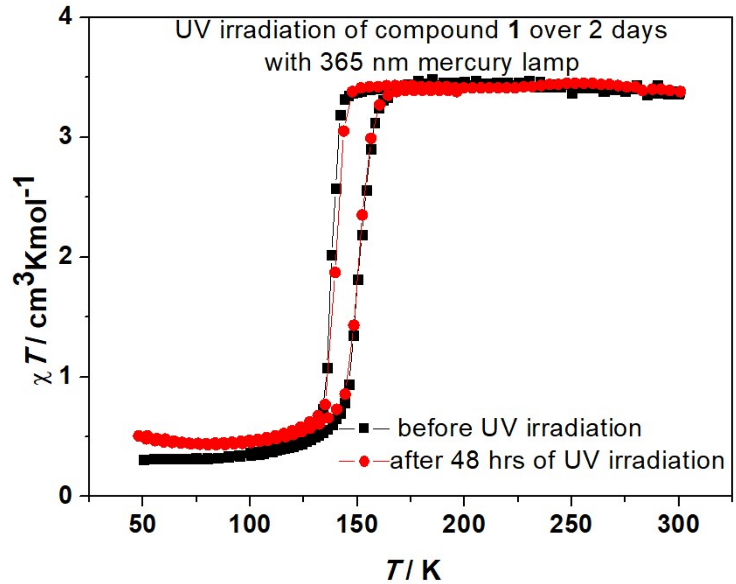
(a)



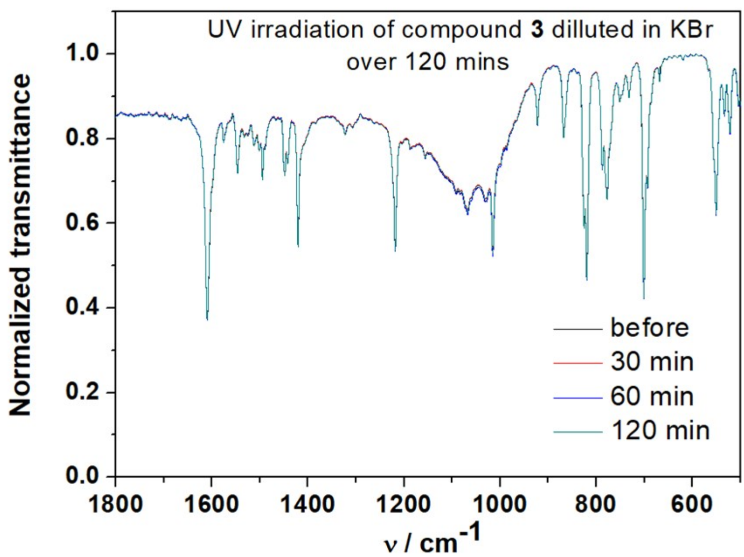
(b)



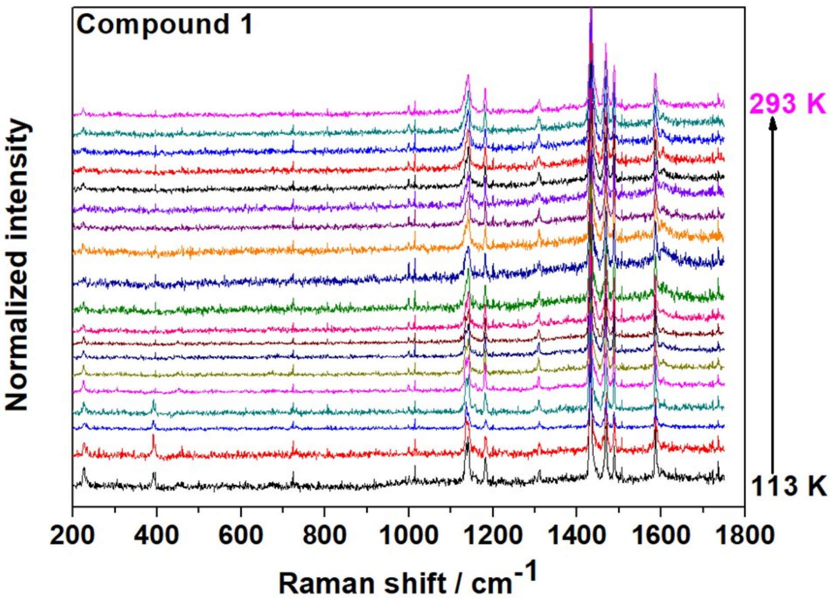
(c)

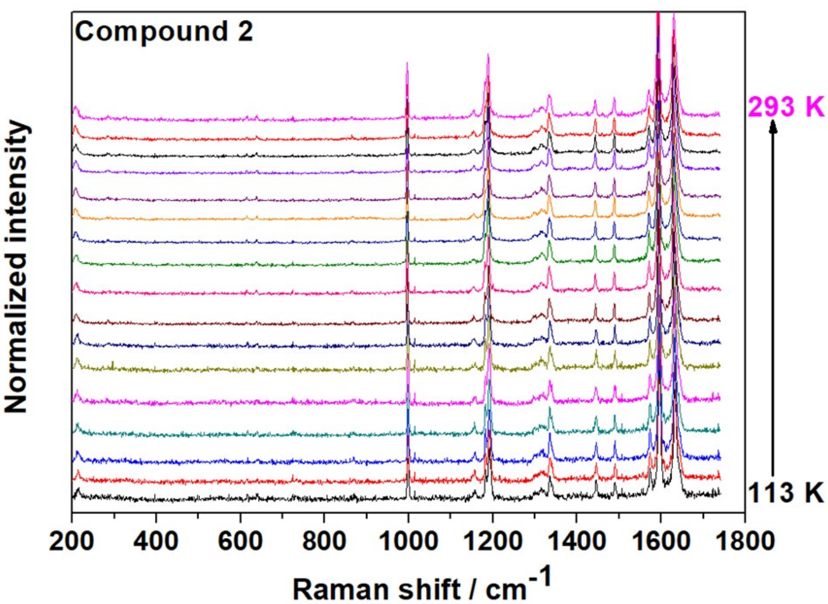


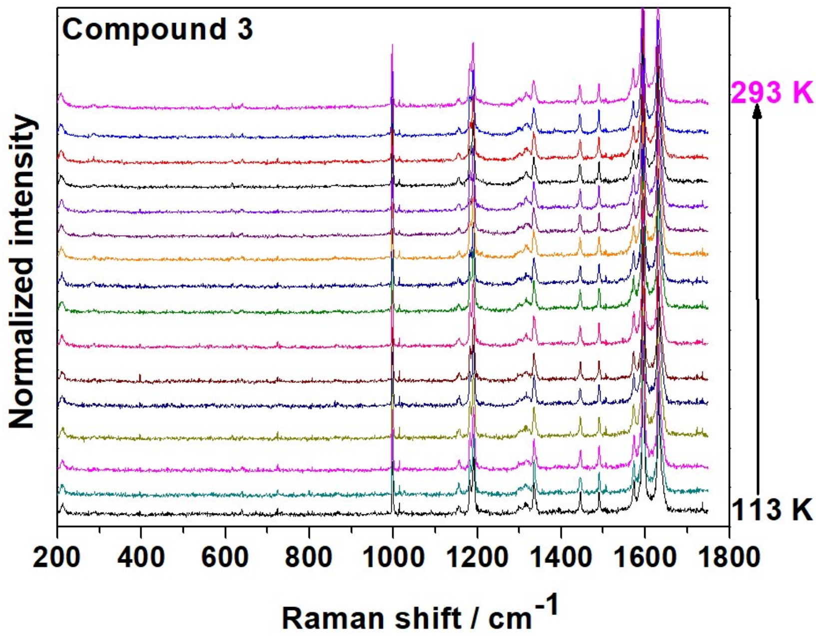
(d)



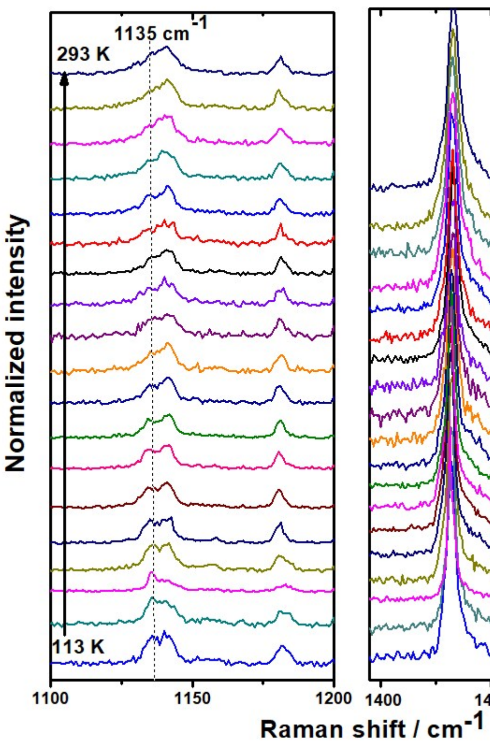
SI-21. UV irradiation experiments with compounds **1** and **3** using different light sources and detection methods: **(a)** Raman spectra of compound **1** collected every 60 min after irradiation by a 375 nm diode; **(b)** UV-VIS measurements of compound **1**: data collected every minute over 120 min under continuous UV irradiation (150 W Xenon light source with UV bandpass filter); **(c)** Magnetic measurements on compound **1** before and after 2 days UV irradiation (mercury lamp, 365 nm); **(d)** FTIR measurements on a KBr pellet of compound **3** over 120 min UV irradiation (150 W xenon light source with UV bandpass filter).


Compound 1
Normalized intensity
293 K
113 K
200
400
600
800
1000
1200
1400
1600
1800
Raman shift / cm-1

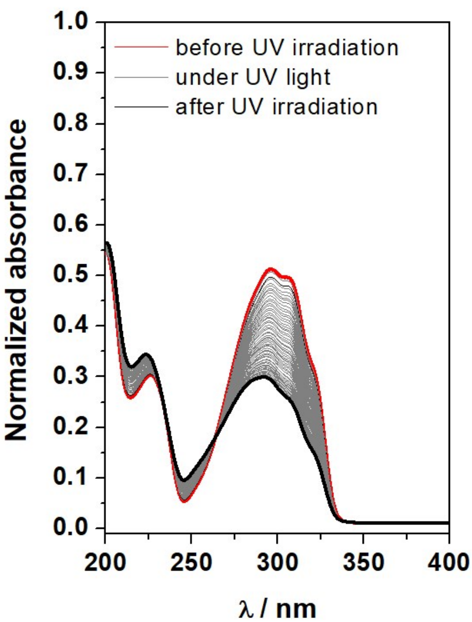

Compound 2
Normalized intensity
293 K
113 K
200
400
600
800
1000
1200
1400
1600
1800
Raman shift / cm-1



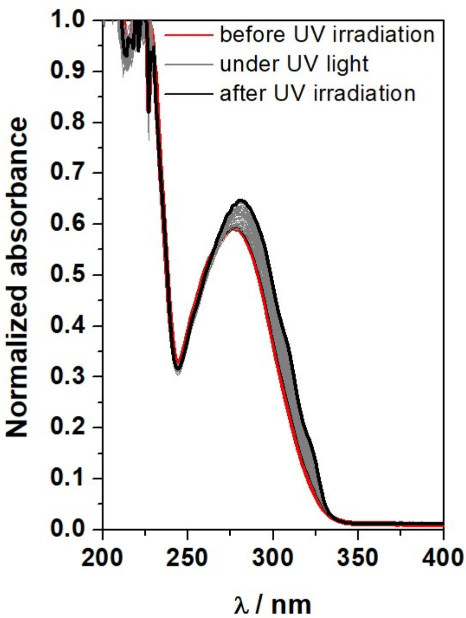
SI-22. Variable temperature 355 nm Raman spectra collected for compounds **1-3.**



SI-23. Temperature dependent Raman spectra (355 nm laser source) of compound **1**. Normalized intensity for two selected regions around 1135 (**left**) and 1506 cm^{-1} (**right**).



(a)



(b)

SI-24. UV-VIS spectra of **(a)** *trans*-stilbene and **(b)** *cis*-stilbene in ethanol before, under and after UV light irradiation (150 W xenon lamp with UV bandpass filter). Data were collected every 15 seconds for 1 hour.

SI-25. Well-distinguishable peaks present in the room-temperature Raman spectra associated with *cis* and *trans*- stilbene measured using different laser sources (355, 532, 785 nm). (N.B. The luminescence of *trans*-stilbene under 355 nm irradiation hides Raman peaks.)

***trans*-stilbene**		***cis*-stilbene**		
532	**785**	**355**	**532**	**785**
1637	1639	1638	1629	1627
1591	1592	1597	1599	1598
1571	1571	1576	1573	1572
1489	1490	1492	1491	
1443	1445	1447	1444	
1337	1338	1336		
1325 1289	1327 1290	1322	1321 1308	1321 1305
		1237	1234	1232
1191	1192	1192	1204	1203
1179	1181	1182	1182	1181
1154	1161	1156		
		1148	1149	1149
			1100	
1024	1026		1029	1029
995 981	997 984	1000	1001	1001
		963 917	966	968
863 851 839	867 855 842			845 770
			752	752
638	640	641		
614	618	618	619	620
		561	561	562 521
	409	401	404	405
286	292		262	260
229	233			