Electronic Supplementary Information

for

X-Ray Crystallographic and Computational Study on Uranyl-Salophen Complexes Bearing Nitro Groups

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Additional details on the crystallographic characterization of complexes 2-6.

COLLECT[1] software was used for the data collection (θ and ω scans) and DENZO-SMN[2] for the processing. The absorption effects were corrected with multi-scan method by SADABS[3] (**3·MeCN**, **4·DMF** and **5·H_2O**) or empirical method by DENZO-SMN[2] (**2·EtOH** and **2·MeOH**). The structures were solved by direct methods with SIR2002[4] and refined by full-matrix least-squares methods with WinGX-software,[5] which utilizes the SHELXL-2013[6] module. All C–H hydrogen positions (except the formyl hydrogens of DMF molecules in **4·DMF** and **6·DMF**) were calculated and refined as a riding atom model with 1.2 or 1.5 times the thermal parameter of the C atoms. The formyl hydrogens in **4·DMF** and **6·DMF** were found from the electron density map and restrained (s = 0.02) to a distance of 0.95 Å from parent C atom with thermal parameter of 1.2 times the C atom parameter. H-atoms bonded to O atoms were also found from the electron density maps, restrained (s = 0.02) to a distance of 0.84 Å from O atoms and their thermal parameters set to values of 1.5 times the O atom parameters. In the structure of **5·H_2O,** PLATON/SQUEEZE[7] was used for a region of electron densities, because it was impossible to refine the present solvent molecule(s) due to high disorder. Anisotropic displacement parameters (ADP, for **4·DMF**) and the geometry (for **2·EtOH**) of the disordered nitroaryl ring atoms were constrained to equal. Also, O atom ADPs of the nitro group in a minor component of **4·DMF** were constrained to equal. For some other disordered atoms, the ADPs were restrained to be more similar (for **2·EtOH** and **4·DMF**, s1= 0.01 and s2 = 0.02) and also more isotropic **2·EtOH**, s = 0.01 or 0.005). Furthermore, some of the atom distances in disordered moieties of the complexes were restrained to be rational (for **2·EtOH**, s= 0.01 or 0.02; **4·DMF**, s = 0.02). In **4·DMF**, the atom ADPs of coordinated dimethylformamide molecule, in **5·H_2O** the ADPs of co-crystallized acetone molecule and in **6·DMF** the ADPs of cocrystallized DMF molecule were restrained to be more similar (s1= 0.01 and s2 = 0.02). Formyl O atoms of cocrystallized DMF molecule in **6·DMF** were also restrained to be more isotropic. Furthermore, the atom distances in acetone and the geometry of uncoordinated water molecule in **5·H_2O**, as well as, the atom distances and geometry of cocrystallized DMF molecule in **6·DMF** were restrained (s = 0.02) to be chemically reasonable.

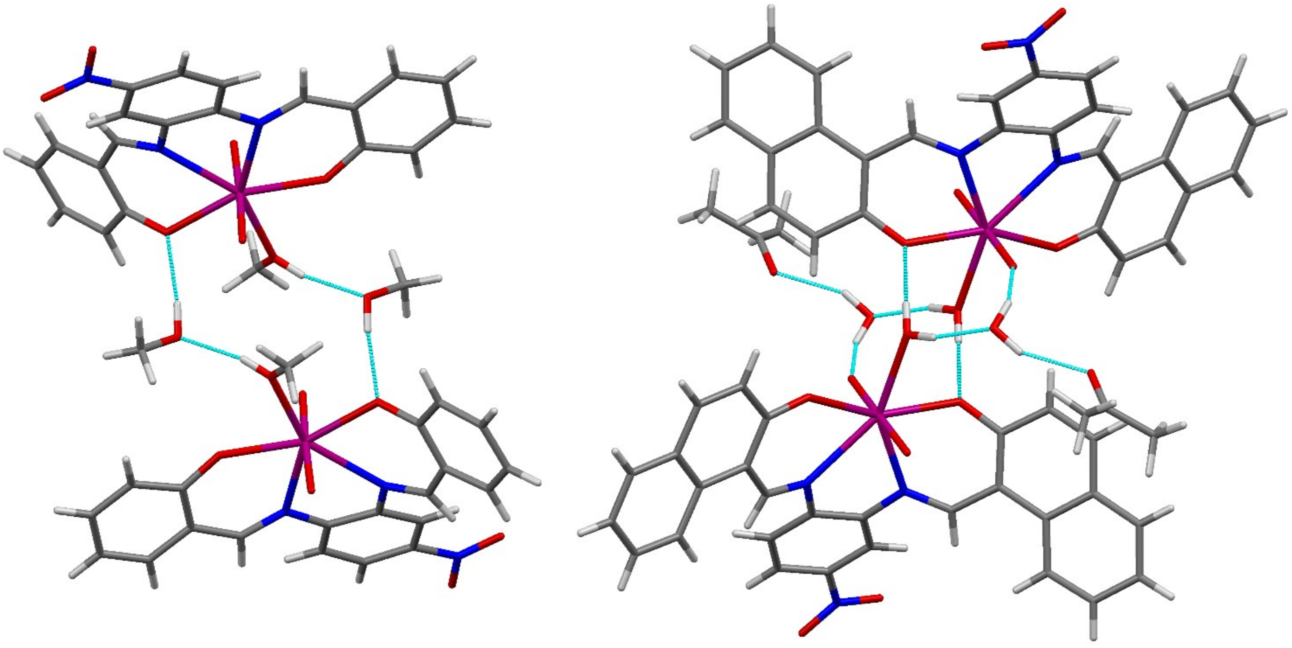

Figure S1. Dimeric structures of the complexes **2·MeOH** and **5·H_2O** showing the connecting hydrogen bonds (color codes: C=gray, H=white, N =blue, O=red, U =purple, H-bond=turquoise).

Table S1. Classical hydrogen bond geometries found from **5·H_2O, 2·MeOH** and**2·EtOH.**

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	<(DHA)
2·MeOH				
(U)-O(Me)-H···O(H)(Me)	0.84(2)	1.80(3)	2.618(8)	165(10)
O(Me)-H···O^{i}	0.84(2)	1.90(3)	2.725(8)	170(9)
2·EtOH				
(U)-O(Et)-H···O^{ii}	0.72(6)	1.91(6)	2.624(4)	170(7)
5·H_2O				
(U)-O(H)-H···O^{i}	0.84(2)	1.84(2)	2.677(5)	173(7)
(U)-O(H)-H···O(H_2)	0.83(2)	1.80(2)	2.611(7)	166(6)
O(H)-H···O(=C(CH_3)$_2$)	0.89(2)	1.93(2)	2.757(11)	154(5)
O(H)-H···O(=U)^{i}	0.89(2)	2.04(4)	2.832(7)	148(6)

Symmetry operations: ^{i} -x+1,-y+1,-z+1; ^{ii} -x+1,-y,-z+2

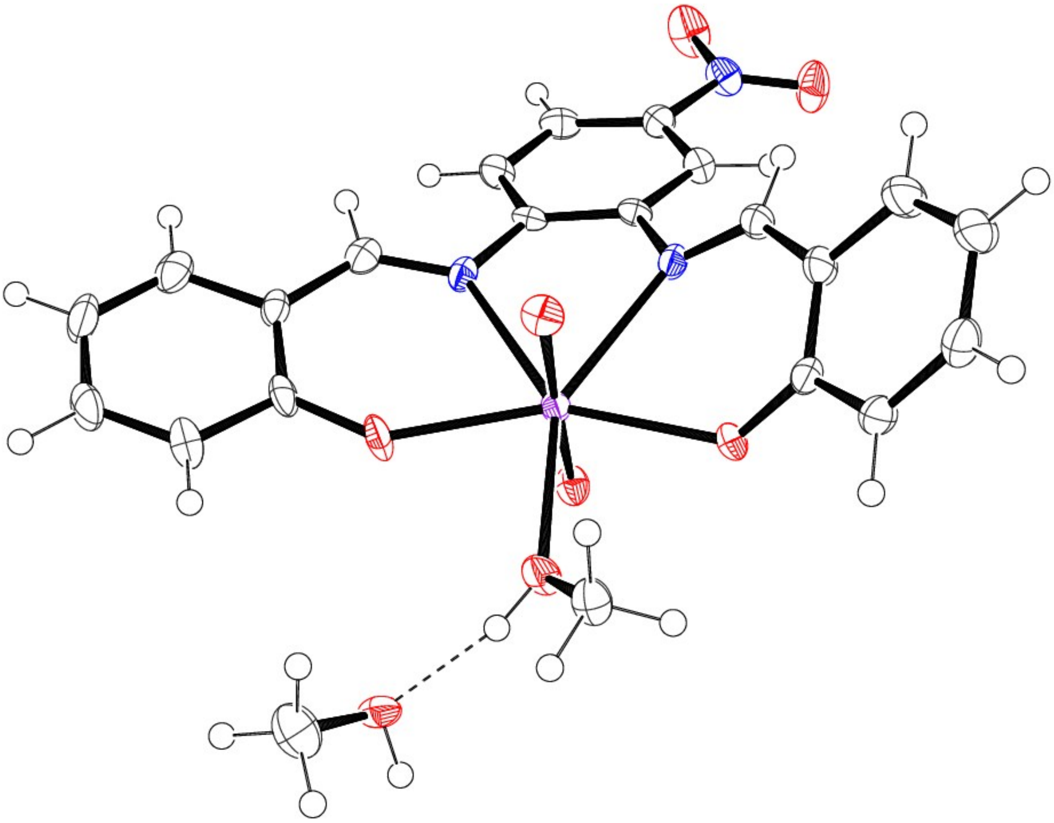

Figure S2. Ortep of **2·MeOH** with 50 % ellipsoid probability (color codes: C=gray, H=black circles, N=blue, O=red, U=purple, H-bond=dashed line).

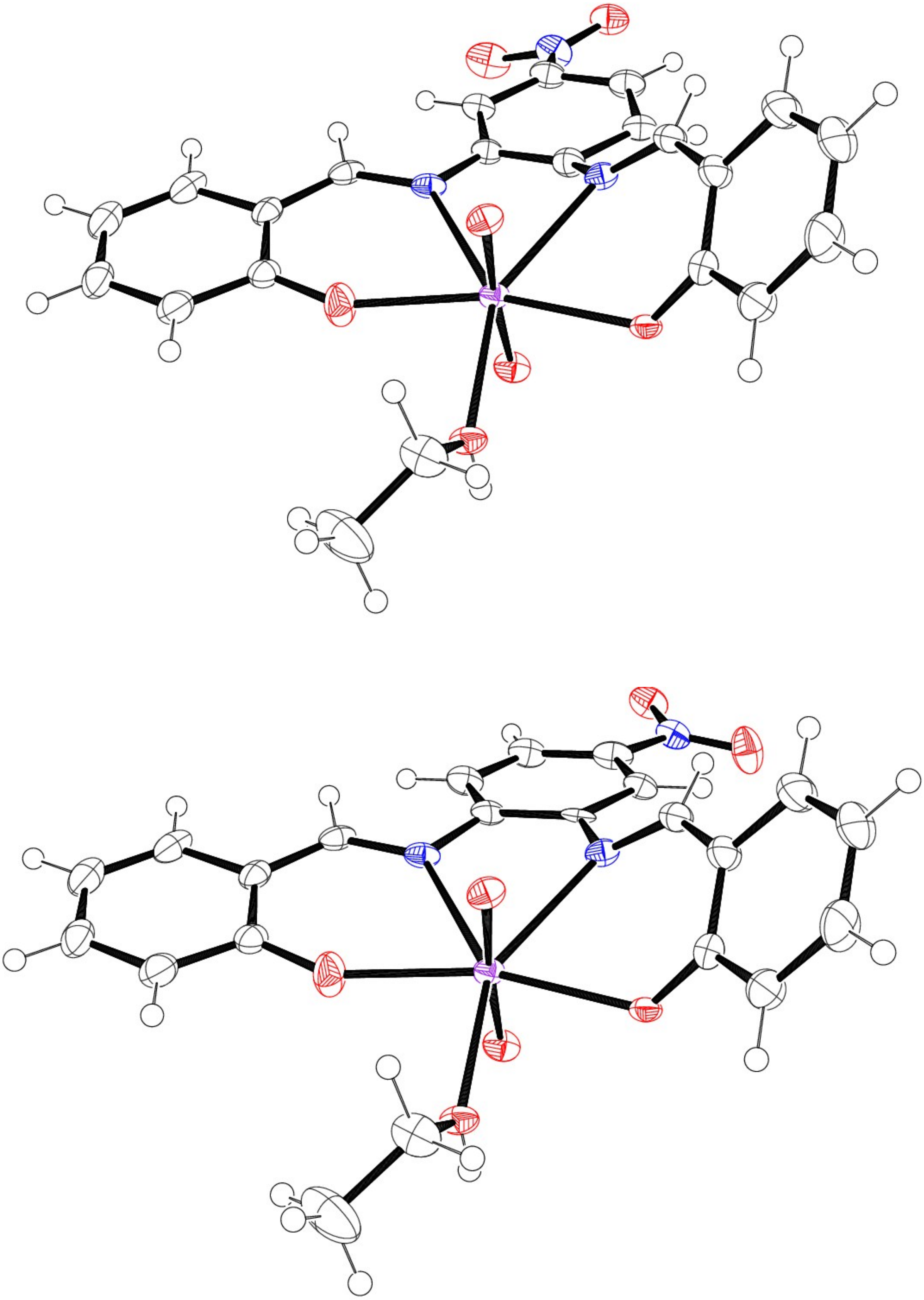

Figure S3. Ortep of **2·EtOH** and its major (top) and minor (below) components with 50 % ellipsoid probability (color codes: C=gray, H=black circles, N=blue, O=red, U=purple).

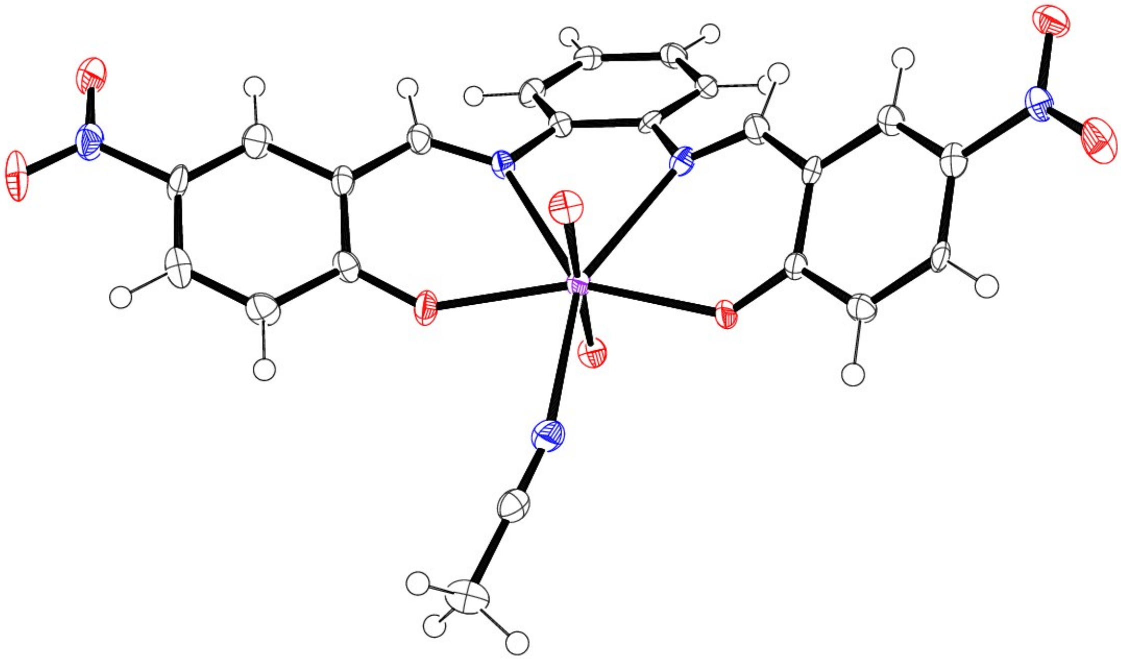

Figure S4. Ortep of **3·MeCN** with 50 % ellipsoid probability (color codes: C=gray, H=black circles, N=blue, O=red, U=purple).

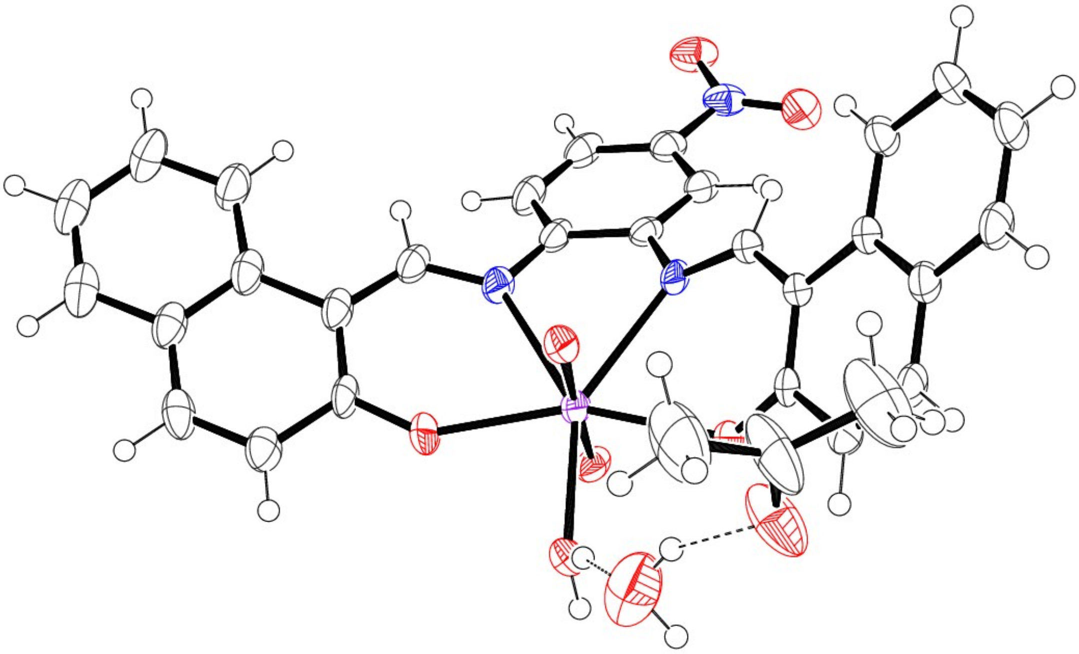

Figure S5. Ortep of **5·H$_2$O** with 50 % ellipsoid probability (color codes: C=gray, H=black circles, N=blue, O=red, U=purple, H-bond=dashed line).

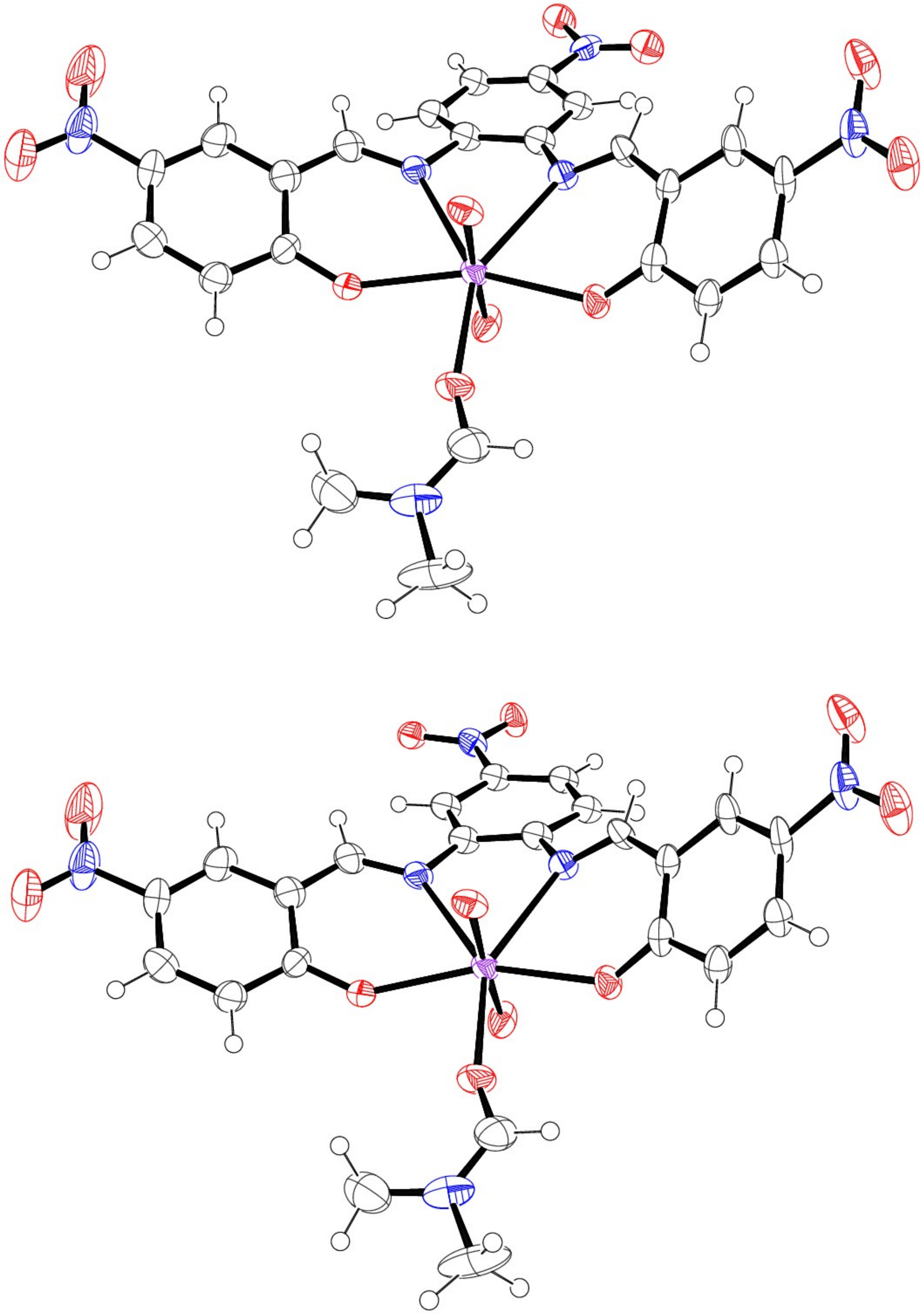

Figure S6. Ortep of **4·DMF** and its major (top) and minor (below) components with 50 % ellipsoid probability (color codes: C=gray, H=black circles, N=blue, O=red, U=purple).

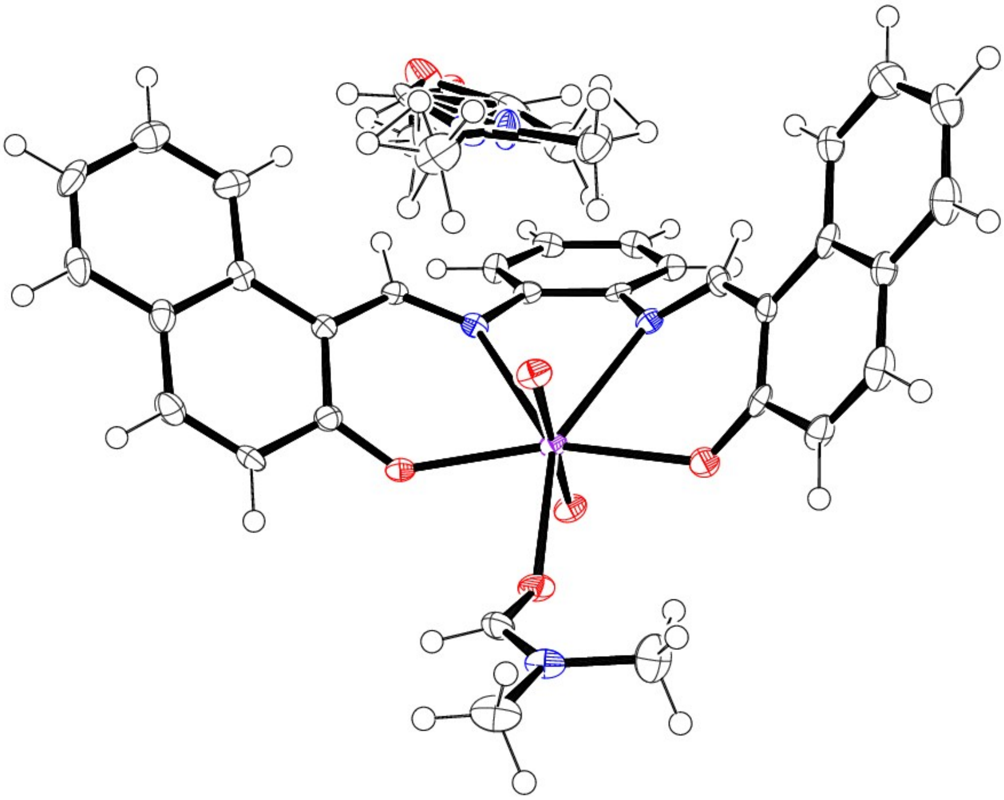

Figure S7. Ortep of **6·DMF** with 50 % ellipsoid probability (color codes: C=gray, H=black circles, N=blue, O=red, U=purple).

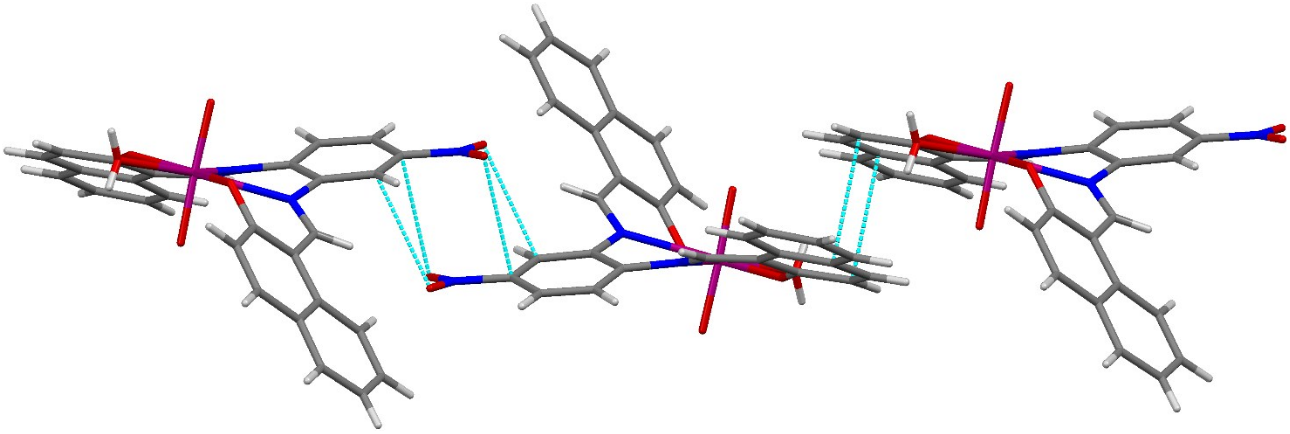

Figure S8. Two stacking interactions found in **5·H$_2$O** showing the closest intermolecular contacts between atoms. The first on the left between nitroaryl moieties (symmetry operation -x, -y, 1-z) has a close C···O contact of 3.16 Å, while the second on the right between naphthalene moieties (symmetry operation 1-x, -y, 2-z) shows close contacts of C···C 3.31 Å and C$_g$···C$_g$ 3.61 Å. Color codes: C=gray, H=white, N =blue, O=red, U =purple, contact=turquoise.

Table S2. Crystallographic data and parameters.

	2·MeOH	**2·EtOH**	**3·MeCN**	**4·DMF**	**5·H$_2$O**	**6·DMF**
CCDC	1519432	1519433	1519434	1519435	1519436	1519437
Formula	$C_{22}H_{21}N_3O_8U$	$C_{22}H_{19}N_3O_7U$	$C_{22}H_{15}N_5O_8U$	$C_{23}H_{18}N_6O_{11}U$	$C_{59}H_{48}N_6O_{17}U^b$	$C_{34}H_{32}N_4O_6U$
F_W	693.45	675.43	715.42	792.46	1589.09^b	830.66
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*Pbca*
Unit cell						
a [Å]	7.7986(2)	8.10340(10)	7.80830(10)	8.6139(3)	11.6878(3)	9.7279(2)
b [Å]	11.3229(2)	11.5084(2)	12.8964(2)	12.4803(5)	12.1737(3)	23.6223(3)
c [Å]	13.4185(3)	12.0611(2)	13.0519(2)	13.4843(5)	12.4532(4)	27.0822(3)
α [°]	74.707(2)	94.8897(10)	117.7150(10)	115.801(2)	73.370(2)	90
β [°]	81.9930(10)	90.5348(11)	96.8180(10)	102.929(2)	66.535(2)	90
γ [°]	84.047(2)	91.4276(12)	100.0270(10)	96.343(2)	83.915(2)	90
V [Å^3]	1129.01(4)	1120.27(3)	1115.29(3)	1235.81(8)	1557.31(8)	6223.37(17)
Z	2	2	2	2	1	8
ρ [Mg/m^3]	2.040	2.002	2.130	2.130	1.694^b	1.773
μ [mm^{-1}]	7.243	7.293	7.338	6.644	5.264^b	5.268
F(000)	660	640	676	756	764^b	3232
Crystal size	0.14×0.08×0.04	0.20×0.13×0.06	0.20×0.15×0.12	0.10×0.06×0.04	0.40×0.08×0.03	0.22×0.10×0.07
θ range	2.12−25.24	2.35−25.25	2.72−25.25	2.50−25.25	2.57−25.25	1.72−25.00
Index ranges	$-8\leq h\leq 9$ $-13\leq k\leq 13$ $-16\leq l\leq 16$	$-9\leq h\leq 9$ $-13\leq k\leq 13$ $-14\leq l\leq 14$	$-8\leq h\leq 9$ $-15\leq k\leq 14$ $-15\leq l\leq 15$	$-10\leq h\leq 9$ $-14\leq k\leq 14$ $-16\leq l\leq 16$	$-14\leq h\leq 14$ $-14\leq k\leq 14$ $-13\leq l\leq 14$	$-11\leq h\leq 11$ $-28\leq k\leq 28$ $-32\leq l\leq 32$
Reflections	6897	7084	15413	17012	20447	52552
Data	4081	4045	4040	4476	5620	5450
R_{int}	0.0404	0.0325	0.0667	0.0728	0.0402	0.0827
Restraints / parameters	2 / 317	321 / 359	0 / 326	38 / 377	27 / 409	51 / 467
Completeness to θ [%]	99.6	99.5	99.9	99.9	99.6	99.4
Reflections [$I>2\sigma(I)$]	3750	3877	3521	3676	5050	4291
Goodness-of-fit on F^2	1.065	1.041	1.022	1.032	1.045	1.071
Final R [$I>2\sigma(I)$]	$R_1 = 0.0372$ $wR_2 = 0.0956$	$R_1 = 0.0235$ $wR_2 = 0.0585$	$R_1 = 0.0345$ $wR_2 = 0.0609$	$R_1 = 0.0430$ $wR_2 = 0.0715$	$R_1 = 0.0300$ $wR_2 = 0.0683$	$R_1 = 0.0368$ $wR_2 = 0.0649$
Final R (all data)	$R_1 = 0.0423$ $wR_2 = 0.0988$	$R_1 = 0.0250$ $wR_2 = 0.0595$	$R_1 = 0.0448$ $wR_2 = 0.0636$	$R_1 = 0.0596$ $wR_2 = 0.0754$	$R_1 = 0.0366$ $wR_2 = 0.0710$	$R_1 = 0.0543$ $wR_2 = 0.0699$
Largest peak / hole [e./Å^3]	2.524 / -1.334^a	1.294 / -1.046	0.805 / -0.753	1.089 / -0.966	1.060 / -0.752	0.643 / -0.807

^{a} Highest peak at 0.2988 0.2851 0.4817 (1.09 Å from U1), deepest hole at 0.4269 0.3276 0.3785 (0.88 Å from U1)); ^{b} Formula and values calculated without the squeezed[7] out solvent.

Table S3: Dimensions (***a, b, c*** in Å, α,β,γ in °) of the model's super-cells submitted to MD simulations

	2·MeOH	**2·EtOH**	**3·MeCN**	**4·DMF**	**5·H$_2$O**	YALSOU
a	24.3102	23.3958	23.3756	25.8417	23.4249	12.5727
b	23.0168	22.6458	24.3474	24.9606	25.7928	16.8834
c	24.1222	26.837	24.9064	26.9686	26.1038	18.9578
α	94.8897	74.707	73.37	115.801	117.715	90
β	90.5348	81.993	66.535	102.929	96.818	90
γ	91.4276	84.047	83.915	96.343	100.027	90

Table S4. Relevant Φ angle parameters for CSD entries and complexes **2-6**.

CSD code	averaged ϕ		ϕ	ϕ'	ϕ''	$\lvert \phi' - \phi'' \rvert$
DEYGUK	**100.66**	DEYGUK	108.91	35.36	45.41	**7.0775**
		DEYGUK	100.88	47.05	33.67	
		DEYGUK	91.58	46.69	51.17	
		DEYGUK	101.29	41.36	41.76	
DOZPAK	**104.87**			47.77	35.11	**12.66**
DOZPEO	**141.66**	DOZPEO	139.06	34.77	23.49	**12.385**
		DOZPEO	144.27	16.03	29.52	
DOZPOY	**108.27**			47.71	34.73	**12.98**
DOZPUE	**100.25**			35.23	48.85	**13.62**
ELUFUM	**110.79**			37.63	35.73	**1.90**
ELUGAT	**112.28**	ELUGAT	110.41	34.47	46.90	**14.91**
		ELUGAT	114.15	48.76	31.37	
EWOLAE	**111.65**			39.76	32.68	**7.08**
EWOLEI	**109.82**			29.66	42.45	**12.79**
EWOLOS	**113.50**			28.96	39.80	**10.84**
EWOLUI	**113.24**			45.75	25.18	**20.57**
EWOLIM	**103.40**			41.47	41.47	**0.00**
EWOMAF	**125.35**	EWOMAF	123.00	29.28	25.78	**6.57**
		EWOMAF	127.71	35.18	25.54	
FITKIC	**121.82**			41.01	26.94	**14.07**
FITKIC10	**121.82**			40.96	26.81	**14.15**
GOKVOT	**104.55**			43.51	36.94	**6.57**
HAJNOV	**113.19**			37.34	37.85	**0.51**
HENWIH	**110.42**			41.72	41.38	**0.34**
HEYXEP	**120.45**			24.04	44.25	**20.21**
HEYXIT	**99.135**	HEYXIT	104.56	51.94	43.52	**4.55**
		HEYXIT	93.71	44.67	45.35	
HEYXOZ	**119.97**	HEYXOZ	122.50	30.27	27.97	**2.22**
		HEYXOZ	122.17	30.44	27.49	
		HEYXOZ	122.84	28.85	29.82	
		HEYXOZ	122.39	27.71	30.37	
HEYXUF	**93.13**			47.86	54.51	**6.65**
HEYYAM	**111.53**			32.93	44.52	**11.59**
ISIWIR	**111.87**			36.70	34.06	**2.64**
KIRHEY	**122.64**			20.02	44.75	**24.73**
LADCUO	**102.06**			44.62	44.51	**0.11**
NICQAS	**100.02**	NICQAS	103.64	38.33	54.54	**9.68**
		NICQAS	96.14	39.81	42.96	
NICQEW	**99.96**	NICQEW	100.89	50.75	47.45	**7.0175**
		NICQEW	109.49	43.71	42.26	
		NICQEW	98.30	45.22	37.57	
		NICQEW	91.18	32.50	48.17	
NICQIA	**103.48**			42.92	41.93	**0.99**
NOGSOS	**92.81**			55.73	38.97	**16.76**
NOGSUY	**107.29**			36.71	36.78	**0.07**
OGOKIF	**101.01**			40.63	39.00	**1.63**
PIYCEF	**119.05**			37.87	36.99	**0.88**
PIYCOP	**120.19**			47.30	13.95	**33.35**
QUBMIL	**136.71**			23.14	25.89	**2.75**
QUJGEI	**114.36**	QUJGEI	112.59	29.26	39.48	**9.405**
		QUJGEI	116.13	29.83	38.42	
REPPEJ	**106.20**					
SAJMOG	**108.87**			48.84	33.28	**15.56**
SONTEU	**110.49**			43.91	32.32	**11.59**
WIBTIK	**111.835**	WIBTIK	107.15	34.82	30.81	**4.18**

		WIBTIK	116.52	36.77	41.12	
YALRAF	**120.71**			40.52	26.29	**14.23**
YALREY	**105.15**			37.74	37.22	**0.52**
YALRIN	**101.16**			37.97	38.88	**0.91**
YALROT	**110.025**	YALROT	115.41	37.91	32.31	**15.81**
		YALROT	104.64	52.47	26.45	
YALRUZ	**104.41**		105.23	32.48	42.41	**6.695**
			103.59	37.24	40.70	
YALSAG	**112.05**			38.34	38.34	**0.00**
YALSEK	**112.74**			35.95	35.95	**0.00**
YALSIO	**118.695**	YALSIO	130.88	19.50	29.68	**11.41**
		YALSIO	106.51	45.21	32.57	
YUYKAG	**109.82**			28.02	54.98	**26.96**
1-MeCN YALSOU	**100.13**	YALSOU		41.43	41.43	**0.00**
compound name	averaged ϕ		ϕ	ϕ'	ϕ''	$\mid \phi' - \phi'' \mid$
2-EtOH	**127.1300**			2.9200	53.5100	**50.59**
2-MeOH	**129.2700**			8.9700	42.8200	**33.85**
3-MeCN	**133.4000**			16.6300	34.6900	**18.06**
4-DMF	**130.6400**			20.0300	33.4700	**13.44**
5-H2O	**127.8200**			9.9700	42.8000	**32.83**
6-DMF	**105.0500**			37.5000	45.7100	**8.21**

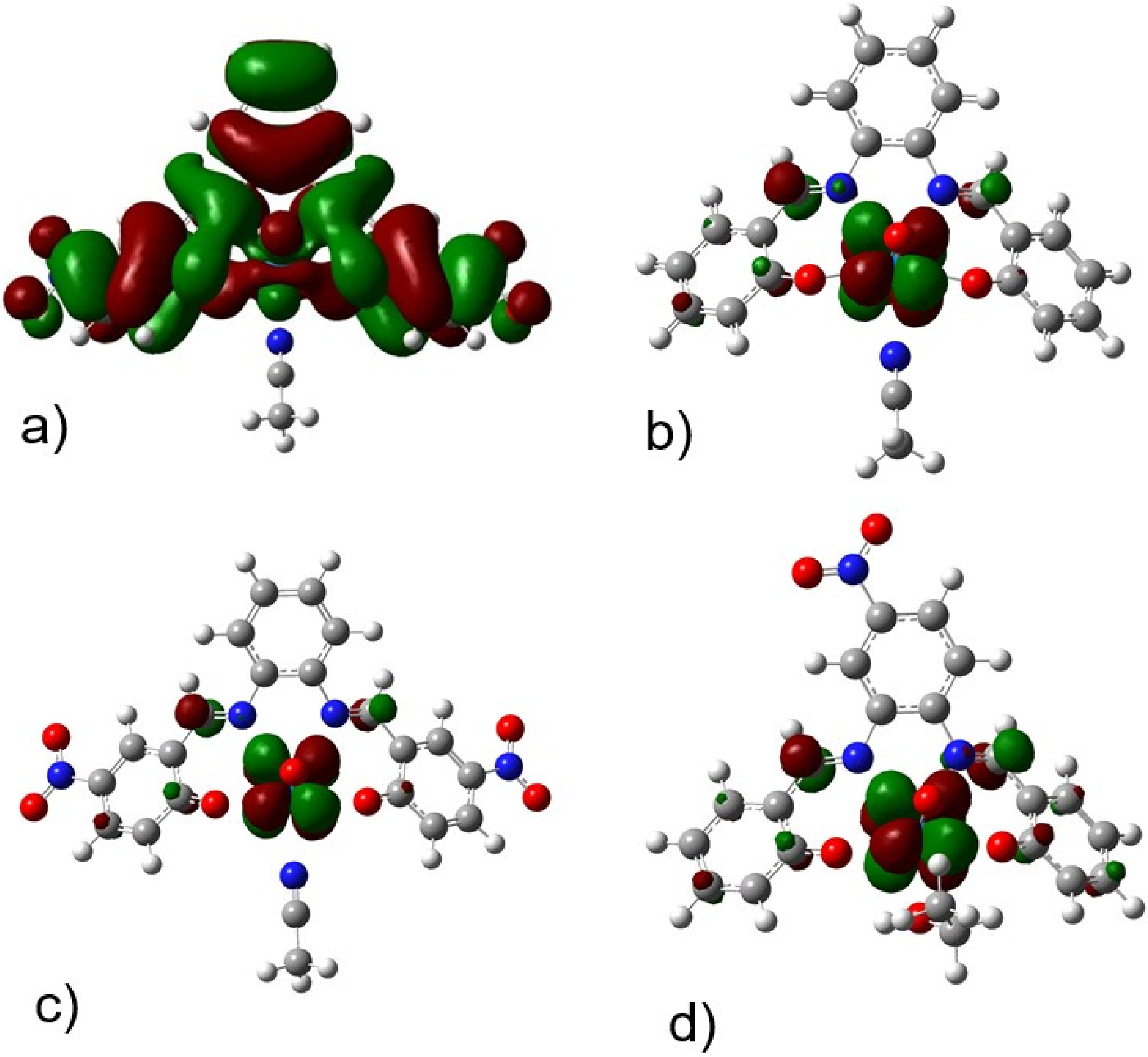

Figure S9. a) **3-MeCN** HOMO isosurface, and LUMO isosurfaces for **1-MeCN** (b), **3-MeCN** (c) and **2-EtOH** (d), showing positive (red) and negative (green) values. Calculated HOMO-LUMO energy differences are 34.2, 34.0 and 35.4 Kcal/mol for **1-MeCN**, **2-EtOH** and **3-MeCN**, respectively**.**

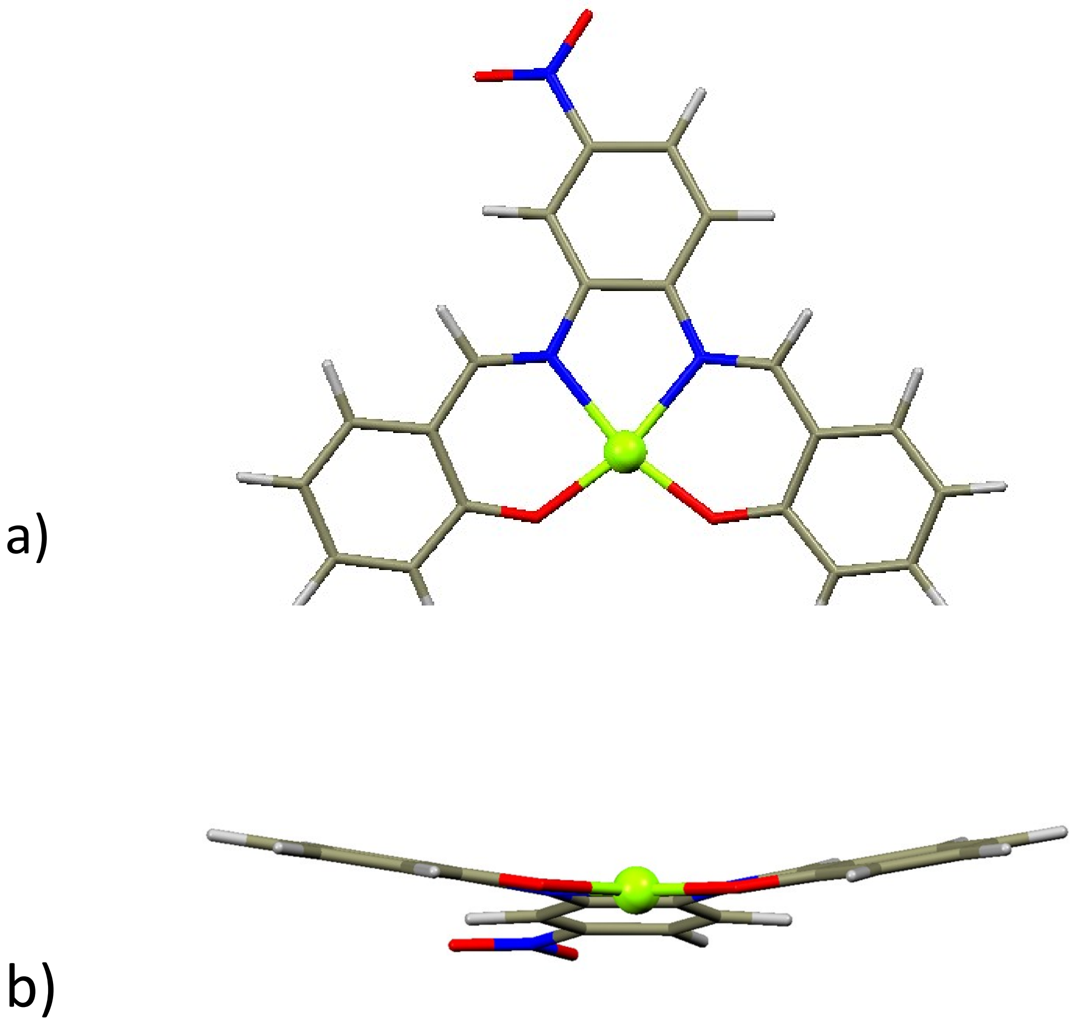

Figure S10. Top a) and side b) views of the calculated structure for the Mg-salophen complex. Φ = 160.70°. Colour code: C = grey, H = light grey, N = blue, O = red, Mg = yellow.

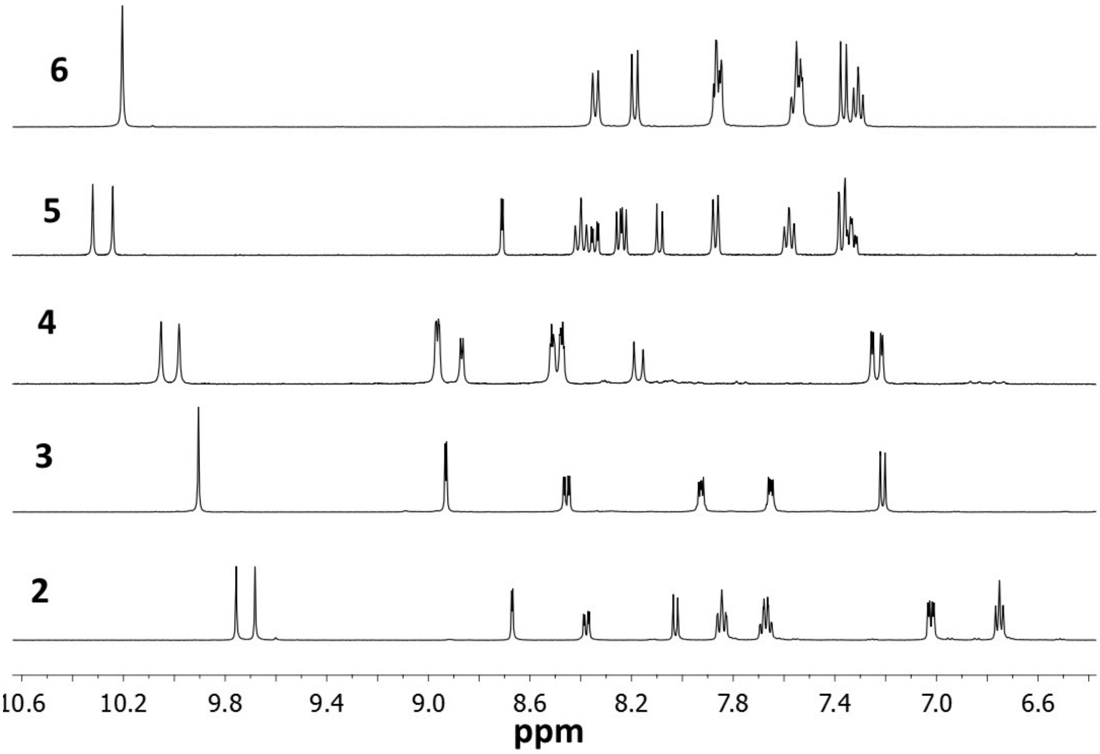

Fig. S11. Portion of the ^{1}H-NMR spectra of complexes **2-6** in DMSO-*d6*.

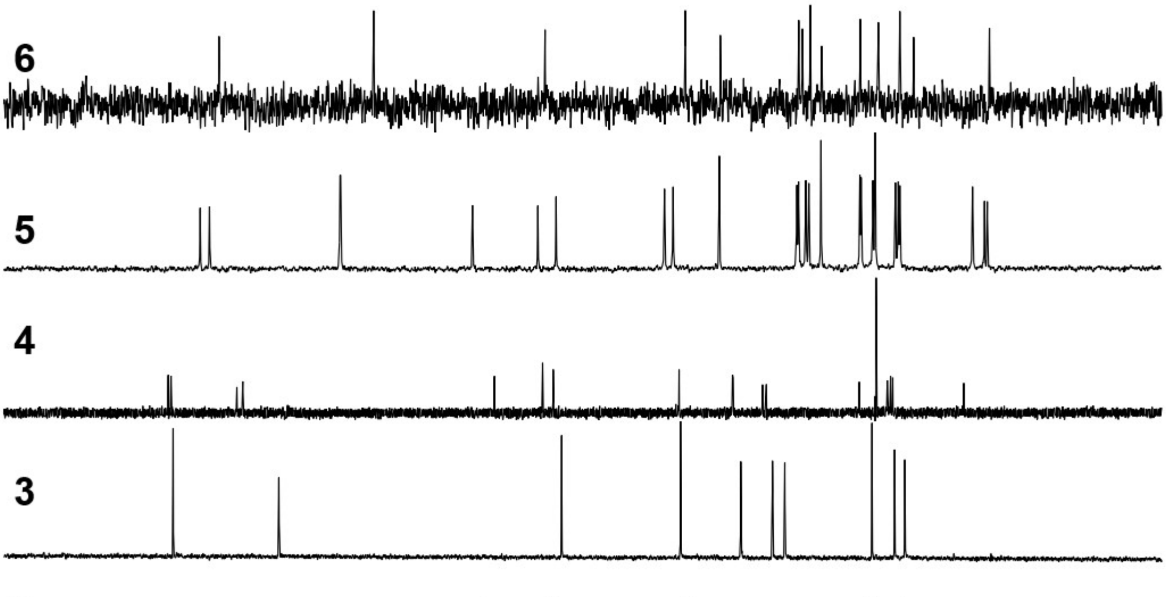

Fig. S12. Portion of the ^{13}C-NMR spectra of complexes **2-6** in DMSO-*d6*.

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