Probing the supramolecular features via π-π interaction of di-iminopyrene-di-benzo-18-crown-6-ether compound: experimental and theoretical study

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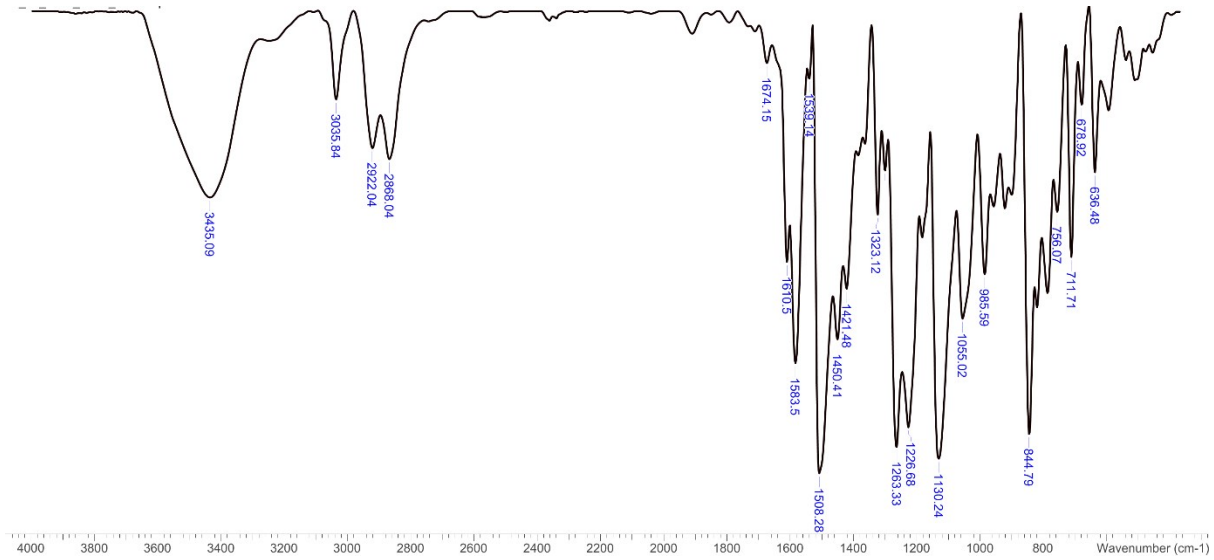

Fig. S1 FTIR spectra of the di-iminopyrene-di-benzo-18-crown-6-ether compound

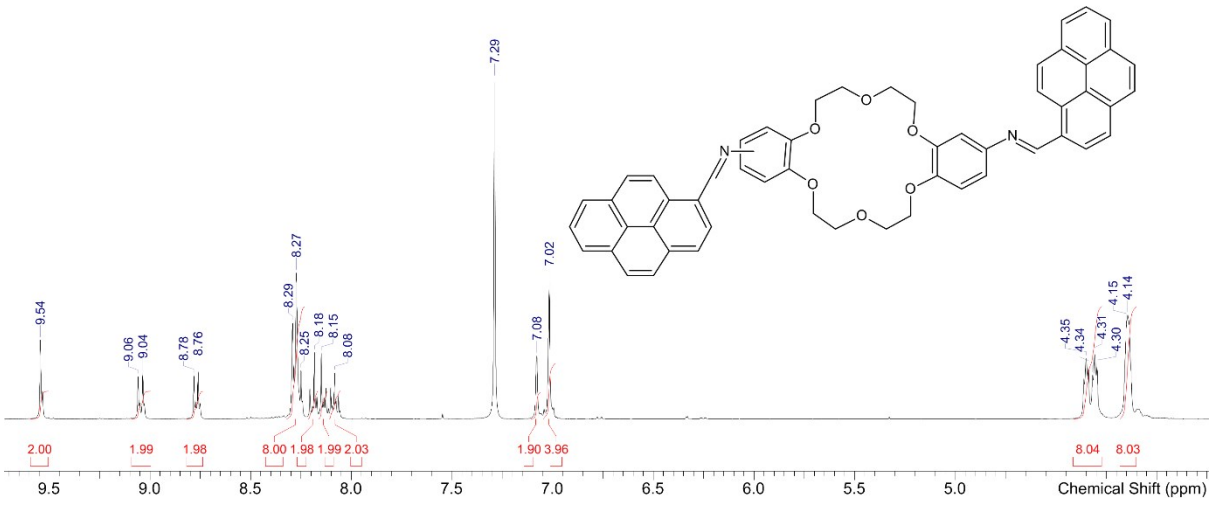

Fig. S2 ^{1}H-NMR spectra of the di-iminopyrene-di-benzo-18-crown-6-ether compound

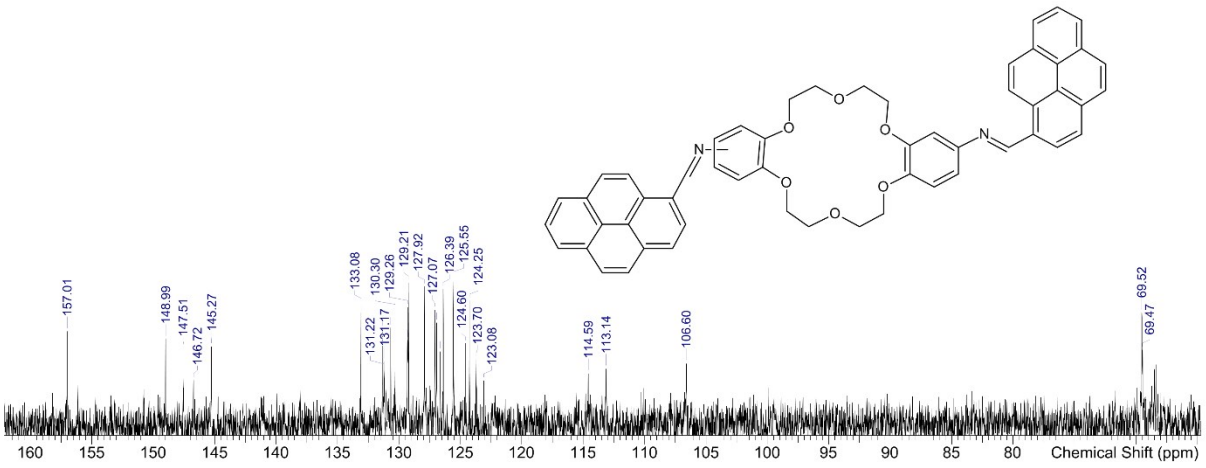

Fig. S3 ^{13}C-NMR spectra of the di-iminopyrene-di-benzo-18-crown-6-ether compound

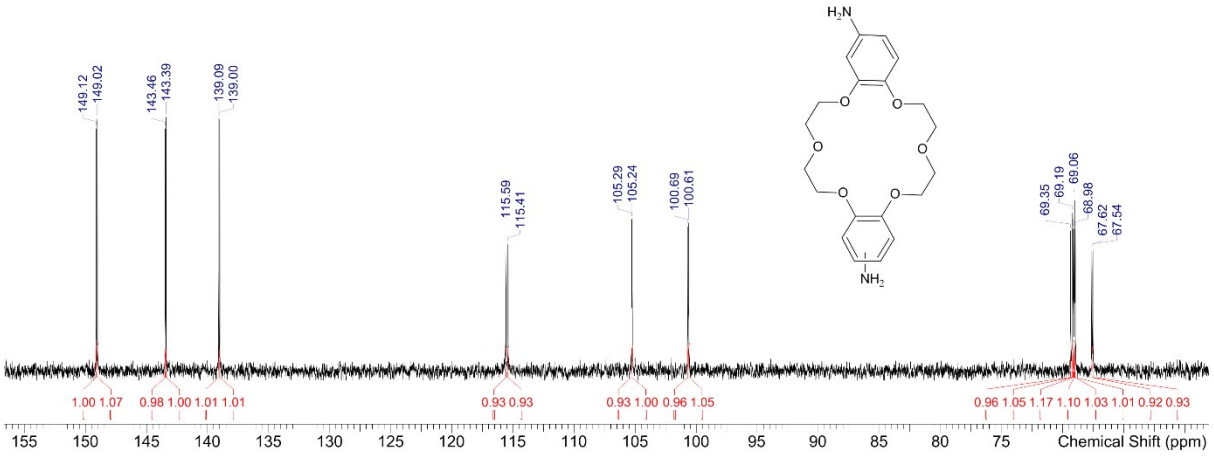

Fig. S4 Quantitative ^{13}C-NMR spectra of the diaminodibenzo-18-crown-6-ether compound

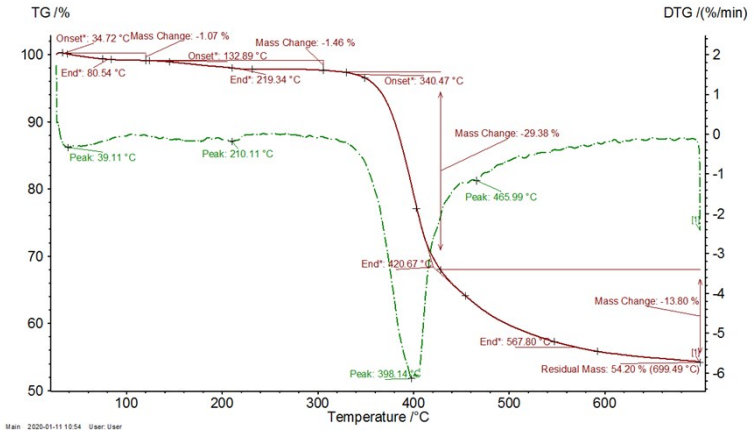

Fig. S5 TGA and DTG curves of the di-iminopyrene-di-benzo-18-crown-6-ether

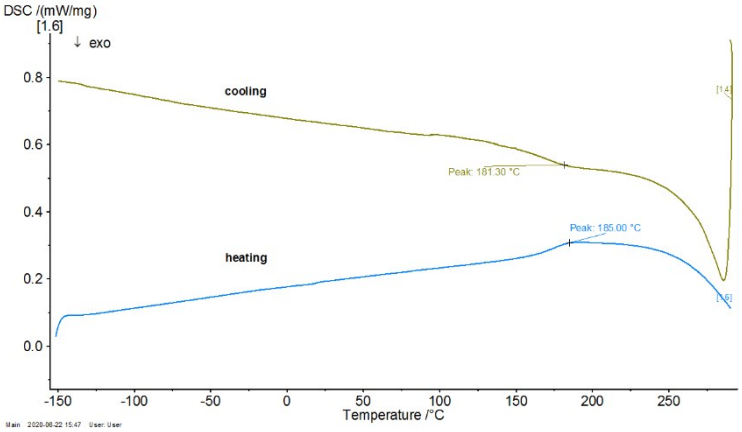

Fig. S6 DSC curves of the di-iminopyrene-di-benzo-18-crown-6-ether

Table S1. Concentrations for the DPyDB-C=N-18C6 compound in different solvents as measured by QCM-D.

	Δf (Hz)	**C (mol/L)**
DPyDB-C=N-18C6 in n-Hexane	-28	5.82×10^{-7}
DPyDB-C=N-18C6 in Toluene	-105	3.25×10^{-6}
DPyDB-C=N-18C6 in 1,2-Dichloroethane	-187	3.86×10^{-6}
DPyDB-C=N-18C6 in Ethanol	-81	2.51×10^{-6}

Table S2. Theoretical values of the oscillator strength values (***f***), calculated at the TD-DFT/6-311++G(d,p) level of theory and experimental of absorption wavelengths (λabs, nm) for the target compounds.

solvent	TD-CAMB3LYP				TD-PBE0				TD-B3LYP				Exp.	
	i1		i2		i1		i2		i1		i2t			
	λ_{abs}	*f*	λ_{abs}	*f*	λ_{abs}	*f*	λ_{abs}	*f*	λ_{abs}	*f*	λ_{abs}	*f*	λ_{abs}	A rel.
gas phase	377.66	1.6309	374.90	1.7835	427.68	1.4170	426.74	1.3719	444.84	1.2768	444.59	1.2210	NA	NA
	370.61	0.4828	370.19	0.2644	421.63	0.1813	421.00	0.1295	438.48	0.1791	438.43	0.1339	NA	NA
	329.40	0272	329.07	0.0262	393.59	0.0000	394.58	0.0000	427.43	0.0000	428.31	0.0000	NA	NA
	316.70	0421	316.13	0.0367	365.67	0.1759	366.18	0.1632	378.47	0.2621	379.20	0.2213	NA	NA
n-hexane	386.56	1.6428	382.78	2.0011	435.70	1.6791	434.17	1.3705	452.74	1.5511	451.95	1.2153	391	0.2255
	380.44	0.7659	379.94	0.3412	431.72	0.2280	427.95	0.4532	448.57	0.2143	444.64	0.4558	372	0.1975
	330.36	0.0520	329.68	0.0468	387.75	0.0001	396.04	0.0000	420.54	0.0000	430.01	0.0000	363	0.2144
	279.35	0.1480	279.27	0.1572	387.70	0.0000	374.17	0.0001	420.08	0.0001	405.24	0.0000	284	0.3412
toluene	388.54	1.6324	384.52	2.0534	437.40	1.7386	435.86	1.3438	454.40	1.6121	453.61	1.1972	396	1.5665
	382.58	0.8391	382.07	0.3523	433.87	0.2384	429.14	0.5555	450.69	0.2231	445.58	0.5499	377	1.4772
	330.60	0.0601	329.77	0.0530	389.02	0.0001	396.31	0.0000	421.55	0.0001	430.31	0.0000	345	0.7905
	271.74	0.3360	276.05	0.0200	334.01	0.0000	339.26	0.0001	352.26	0.0538	351.15	0.0001	290	1.6218
1,2-dichloroethane	387.14	1.6863	382.95	2.1840	435.14	1.7835	433.55	1.2767	451.86	1.6101	450.83	1.1493	396	1.7567
	381.65	0.7669	380.67	0.2003	431.49	0.2132	424.10	0.6596	447.74	0.2520	439.49	0.6459	377	1.7827
	330.12	0.0559	328.99	0.0497	393.42	0.0001	396.59	0.0000	382.58	0.1107	430.55	0.0002	365	1.6492
	278.99	0.1583	278.91	0.1667	341.43	0.0530	341.44	0.0520	348.80	0.0213	366.67	0.0000	288	2.0418
ethanol	385.46	1.7130	381.35	2.1512	433.19	1.7582	431.49	1.2662	449.76	1.5833	448.59	1.1402	390	0.8575
	380.01	0.6972	378.84	0.1885	429.18	0.2082	421.42	0.6428	445.22	0.2514	436.51	0.6317	380	0.8597
	316	0.1111	313	0.0549	367.78	0.0284	366.63	0.0903	380.91	0.1124	380.40	0.1067	289	0.6977
	267.57	0.3594	268.13	0.0234	324.69	0.0000	324.72	0.0080	348.50	0.0218	345.99	0.0000	232	1.2406

NA= no measurement available; A rel. = represents the relative absorbance of the most intense peak as results from experimental spectra.

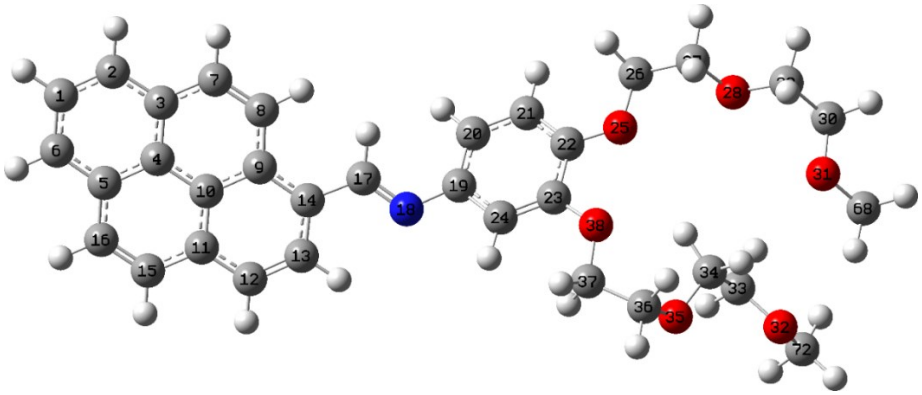

Fig. S7 The molecular system optimized with PBE0/6-311+G(d,p)

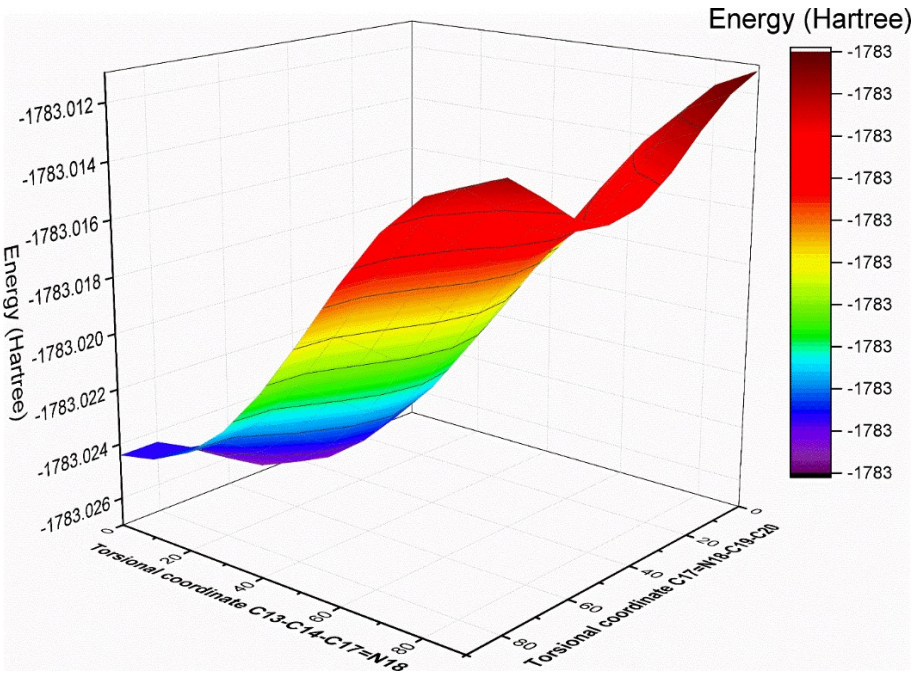

Fig. S8 Potential energy surface scan for the dihedral angles C13–C14–C17=N18 and C17=N18–C19–C20 (labels in agreement with Figure S7) in proposed structure with PBE0/6-311+G(d,p)

Table S3. The energy differences (Hartree) between the **i1** and **i2** position isomers, as well as the dipole moments.

Isomer	Energy	Energy differences (kcal/mol)	μ (D)
i1	-2641.477658	0.42	4.59
i2	-2641.478331	0	4.52

Table S4. Dihedral angle values [°] of **i1** and **i2** isomers computed with PBE0/6-311+G(d,p) method.

Position	Dihedral angle	i1	Dihedral angle	i2
α	C9-C14-C17=N18	175.8	C9-C14-C17=N18	175.2
	C14-C17=N18-C19	176.2	C14-C17=N18-C19	176.2
	C17=N18-C19-C24	145.4	C17=N18-C19-C24	145.1
β	C36-C35-N38=C39	33.3	C35-C34-N38=C39	39.4
	C35-N38=C39-C40	-177.5	C34-N38=C39-C40	-177.1
	N38=C39-C40-C41	3.6	N38=C39-C40-C41	4.8

Table S5. Bond length values [Å] of **i1** and **i2** isomers computed with PBE0/6-311+G(d,p) method.

Position	Bond length	i1	Bond length	i2
α	C14-C17	1.461	C14-C17	1.461
	C17=N18	1.278	C17=N18	1.278
	N18-C19	1.397	N18-C19	1.397
β	C35-N38	1.398	C34-N38	1.400
	N38=C39	1.277	N38=C39	1.277
	C39-C40	1.460	N39-C40	1.461

Table S6. Valence angles values [°] of **i1** and **i2** isomers computed with PBE0/6-311+G(d,p) method.

Position	Valence angle	i1	Valence angle	i2
α	C14-C17=N18	122.0	C14-C17=N18	122.0
	C17=N18-C19	119.6	C17=N18-C19	119.5
β	C35-N38=C39	119.7	C34-N38=C39	119.1
	N38=C39-C40	126.6	N38=C39-C40	126.7

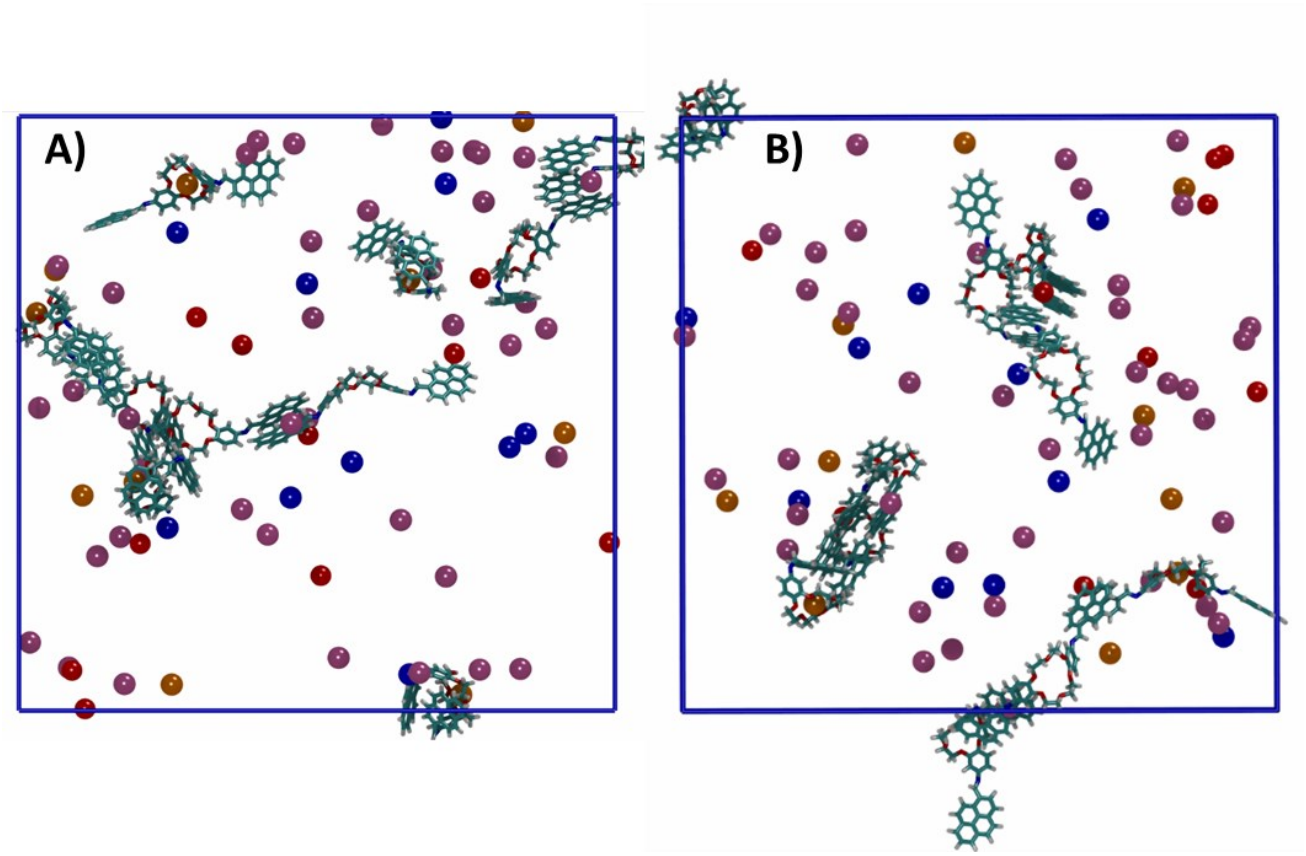

Fig. S9 Final structures obtained after the A) first simulation and B) second simulation of the DPyDB-C=N-18C6 molecules in the ion mixture. Each atom is colored as follows: C atoms are teal, O atoms are red, N atoms are blue, H atoms are white, K^+ atoms are orange spheres, Na^+ atoms are red spheres, Ca^{2+} atoms are blue spheres and Cl^- atoms are purple spheres.