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Bis-isonicotinoyl linkers containing polyaromatic scaffolds: synthesis, structure and spectroscopic properties.

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Supporting information

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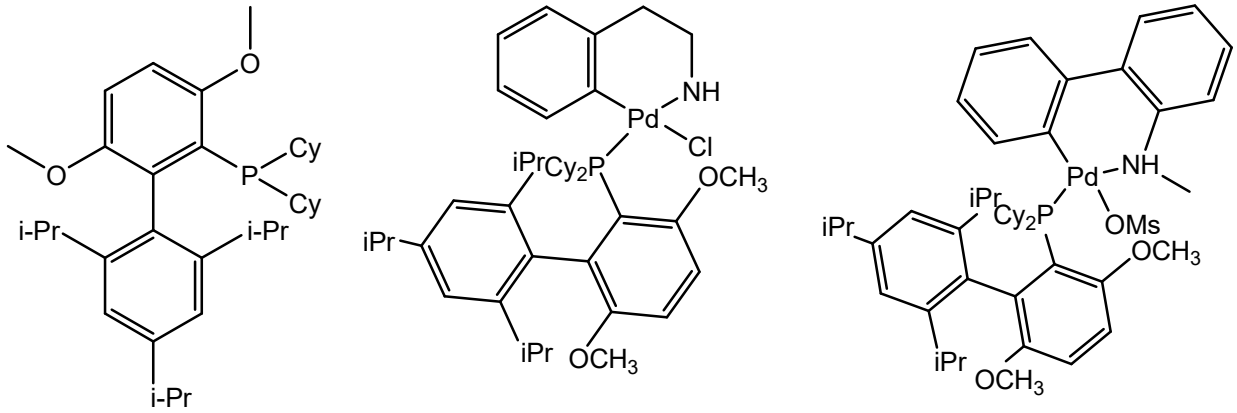
General

Structure of catalysts employed



Scheme S1 Structures of BrettPhos, PdG1 (methyl-t-buthyl ether molecule is omitted) and PdG4

FT-IR spectroscopy

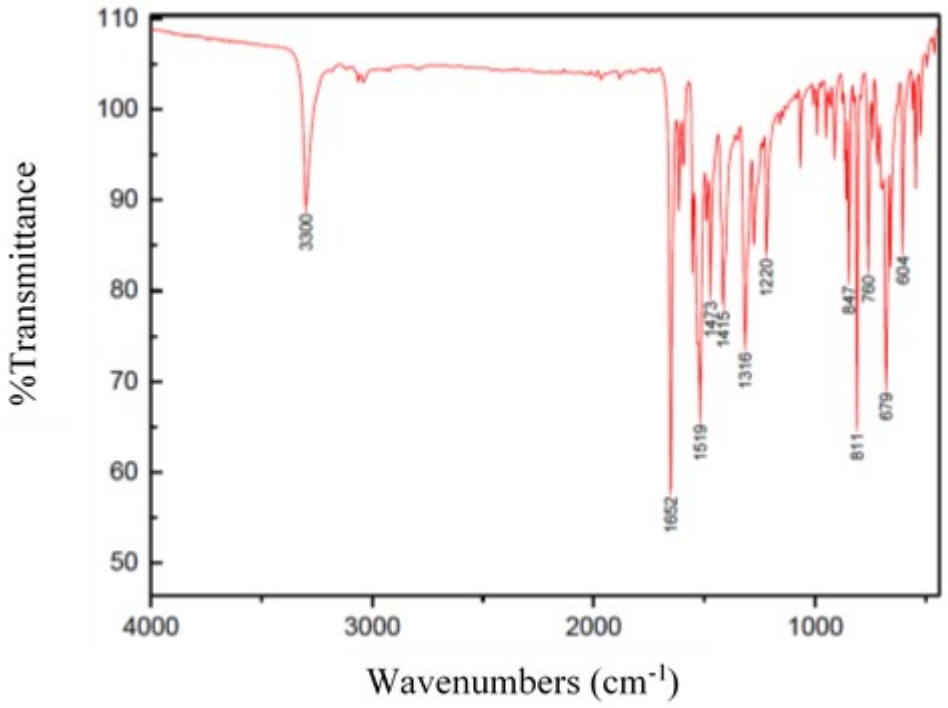


Figure S1 FT-IR spectrum of **1**

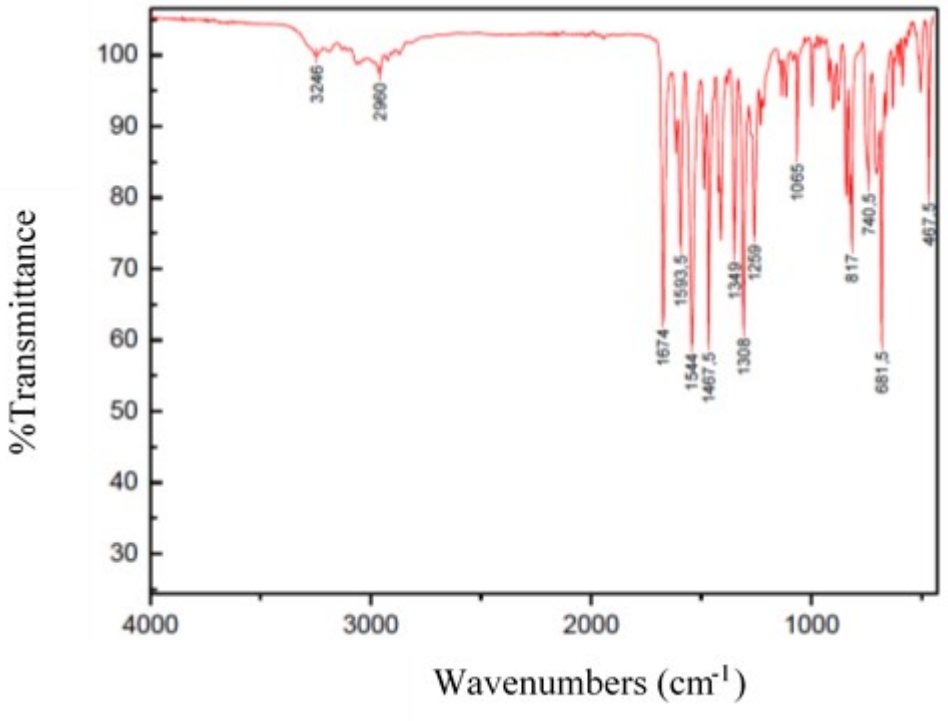


Figure S2 FT-IR spectrum of **2**

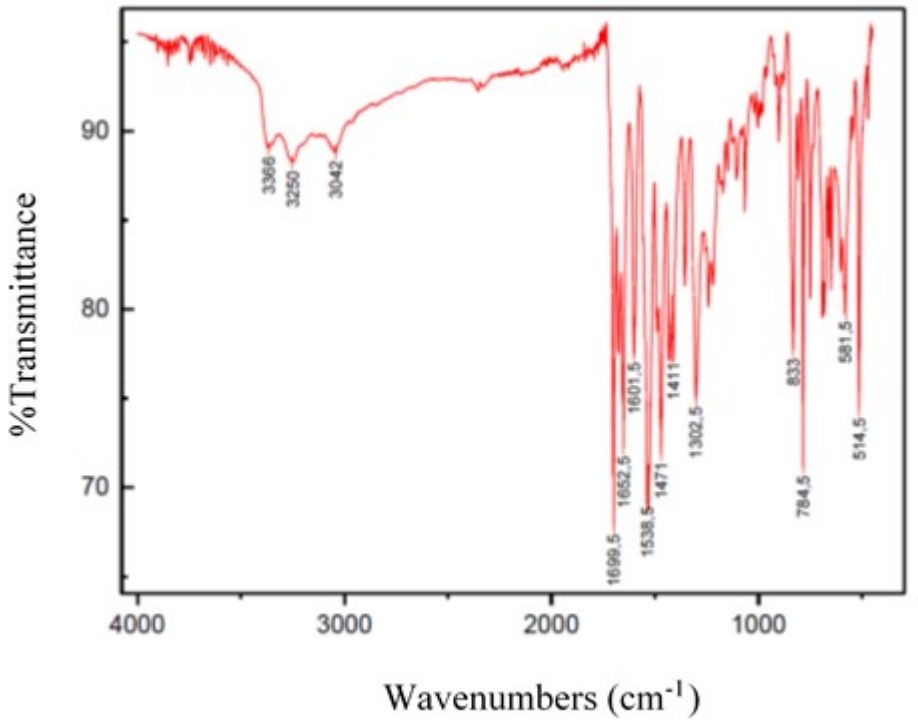


Figure S3 FT-IR spectrum of **3**

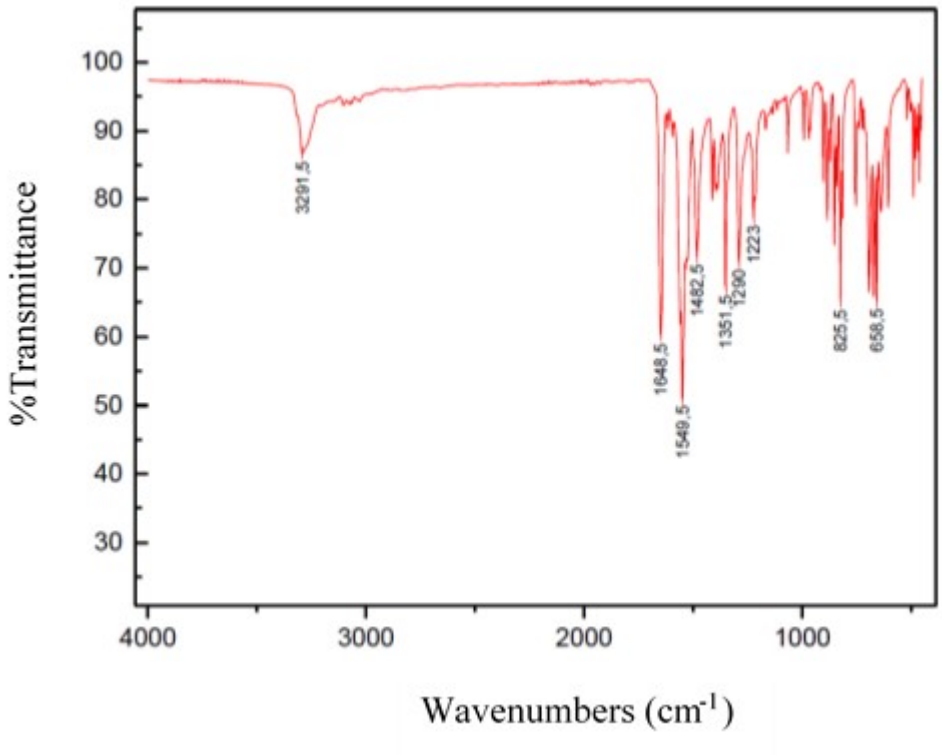


Figure S4 FT-IR spectrum of **4**

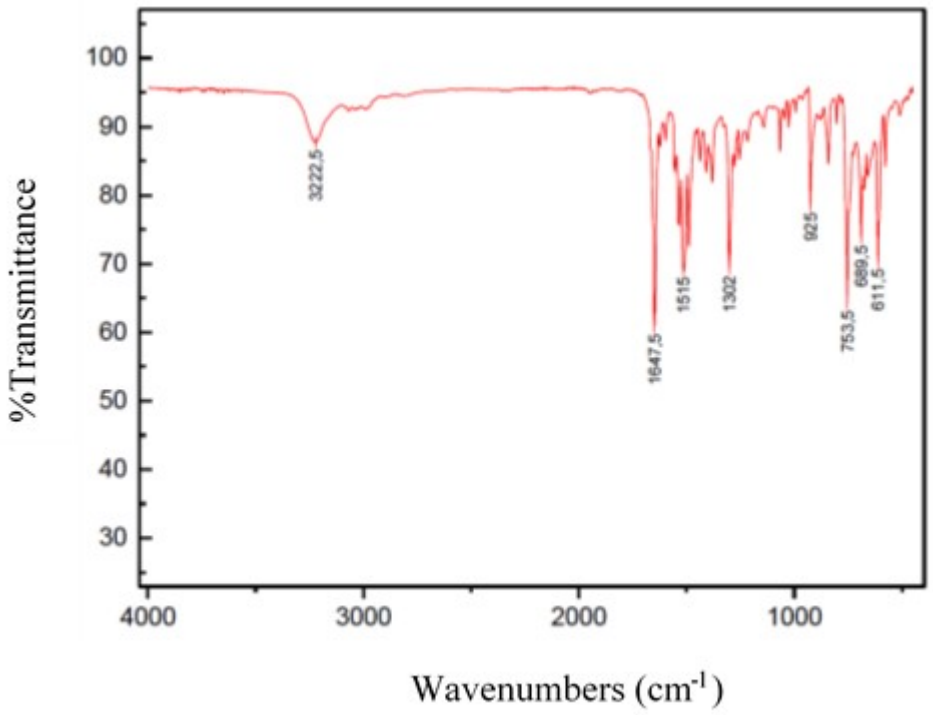


Figure S5 FT-IR spectrum of **5**

[1]HNMR spectroscopy

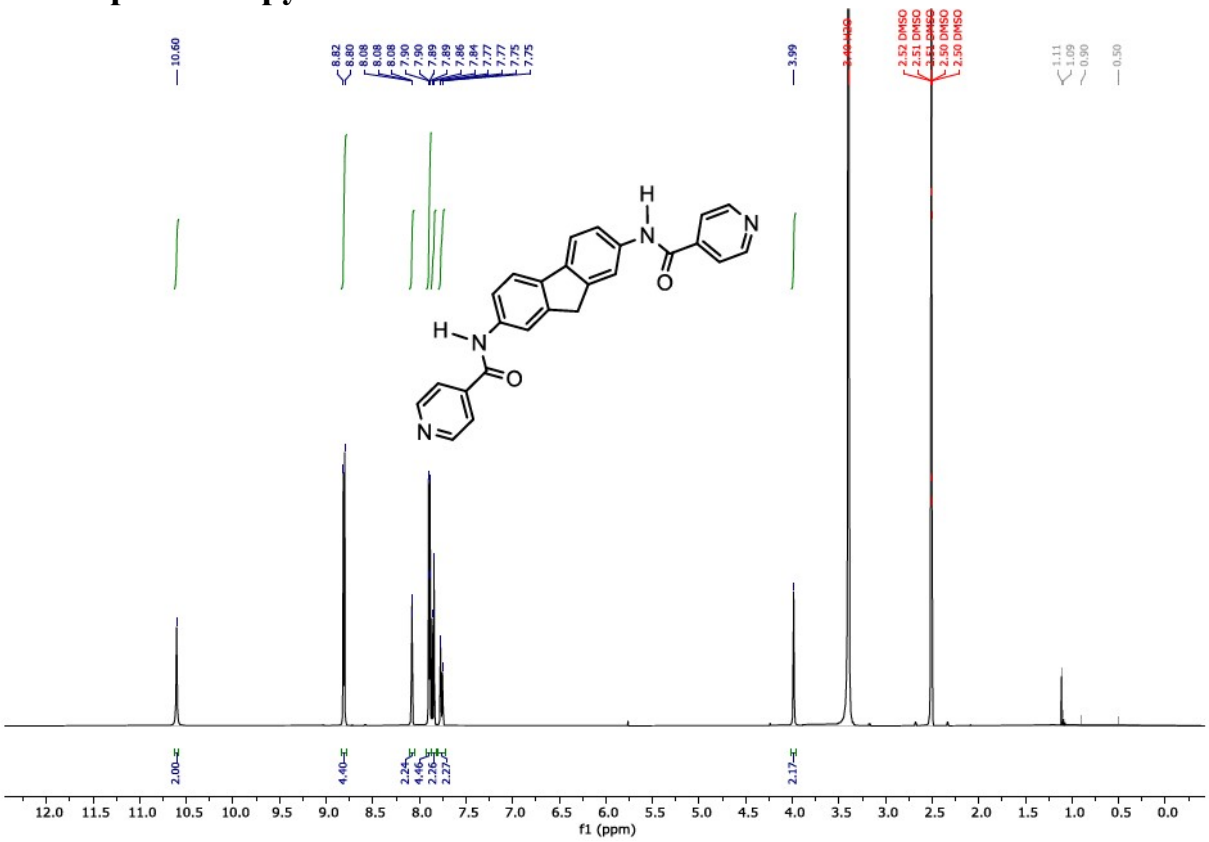


Figure S6 [1]H NMR spectrum of **1** (DMSO-d_6, 400 MHz, 25°C)

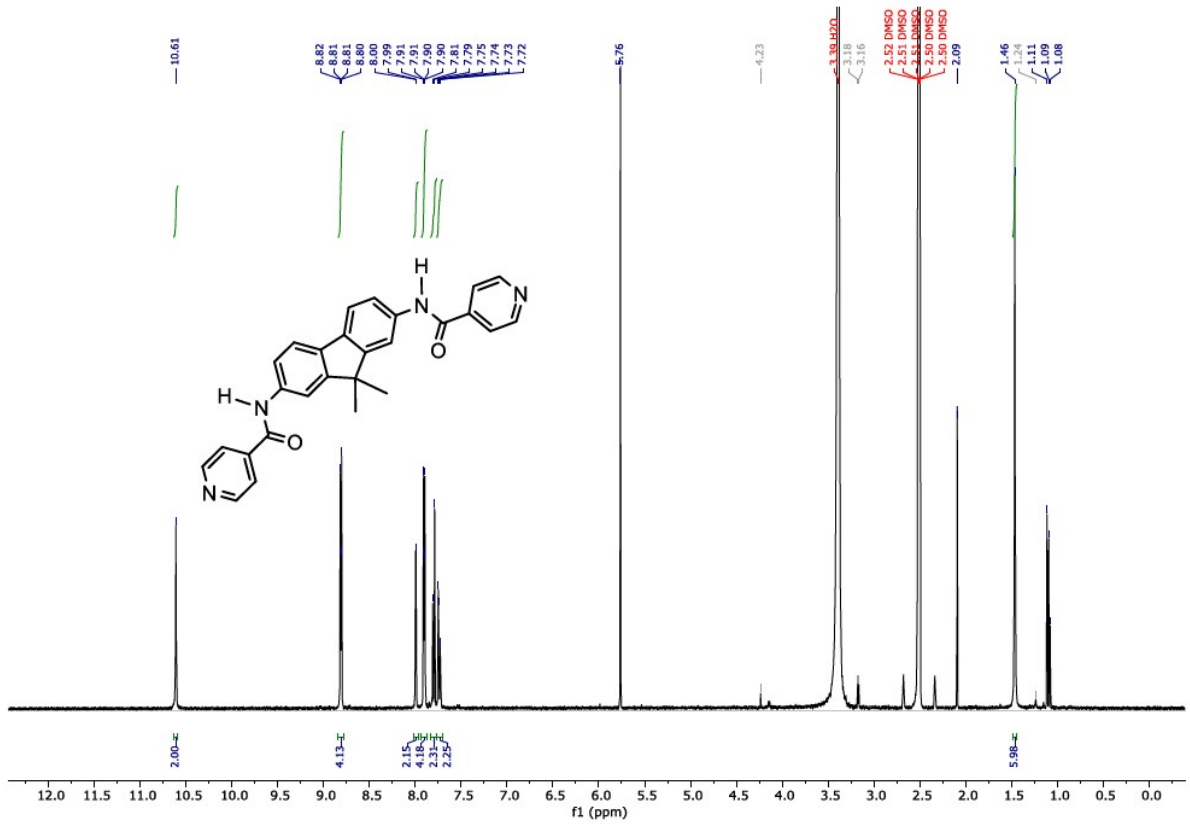


Figure S7 [1]H NMR spectrum of **2** (DMSO-d_6, 400 MHz, 25°C)

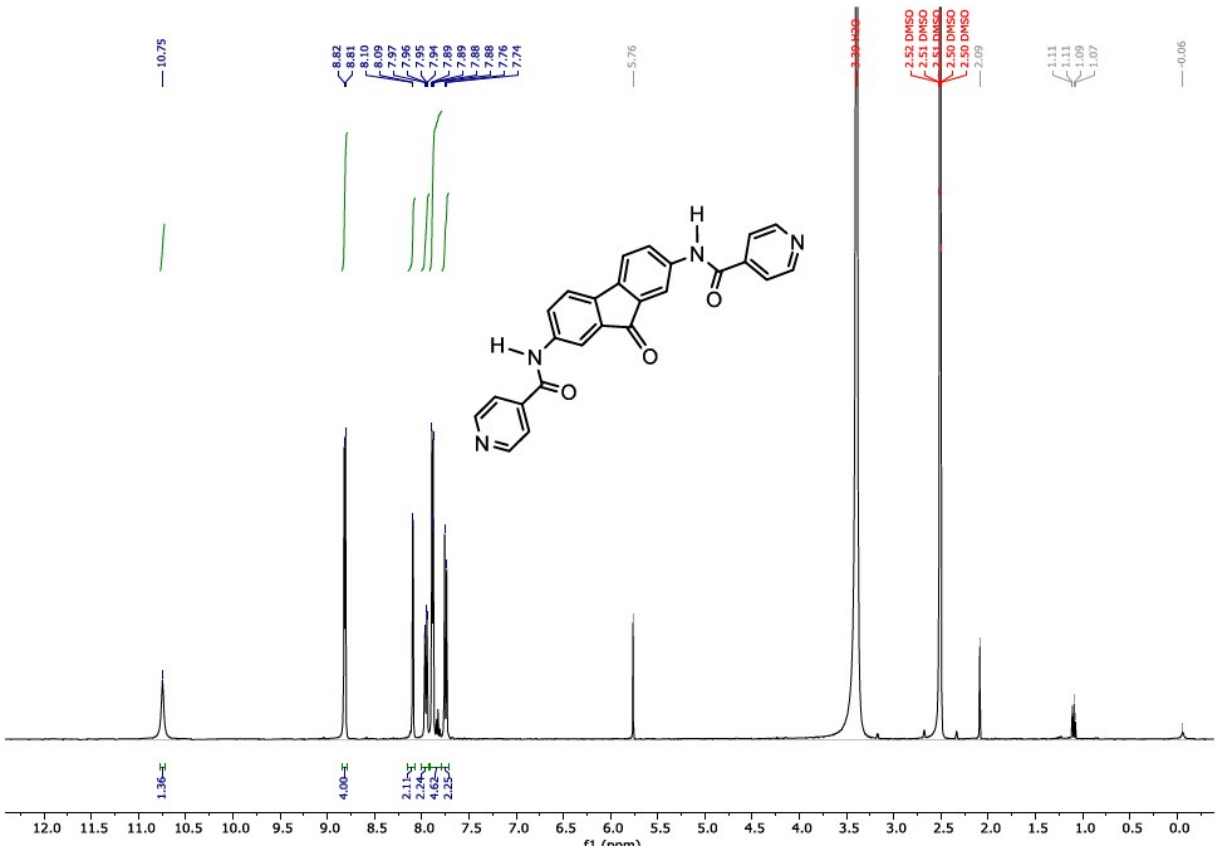


Figure S8 ^{1}H NMR spectrum of **3** (DMSO-d_6, 400 MHz, 25°C)

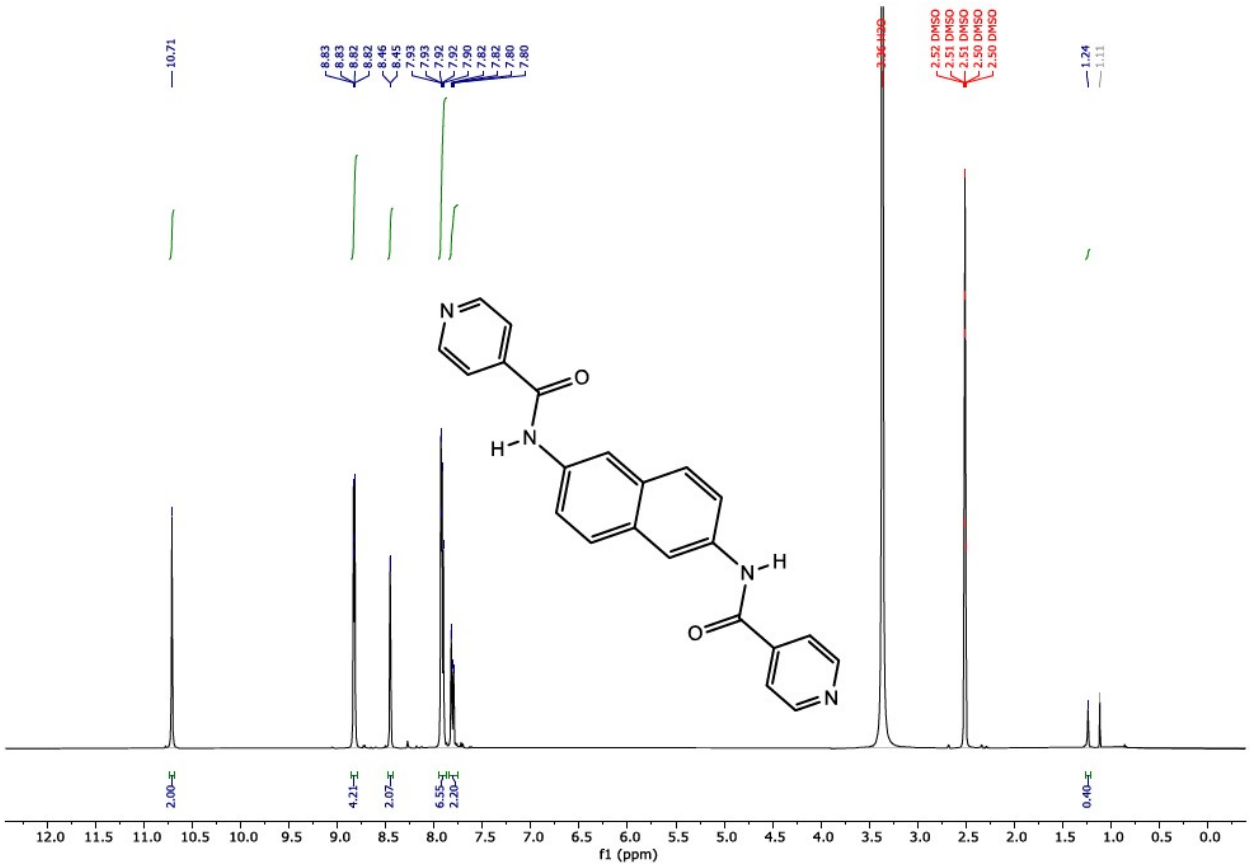


Figure S9 ^{1}H NMR spectrum of **4** (DMSO-d_6, 400 MHz, 25°C)

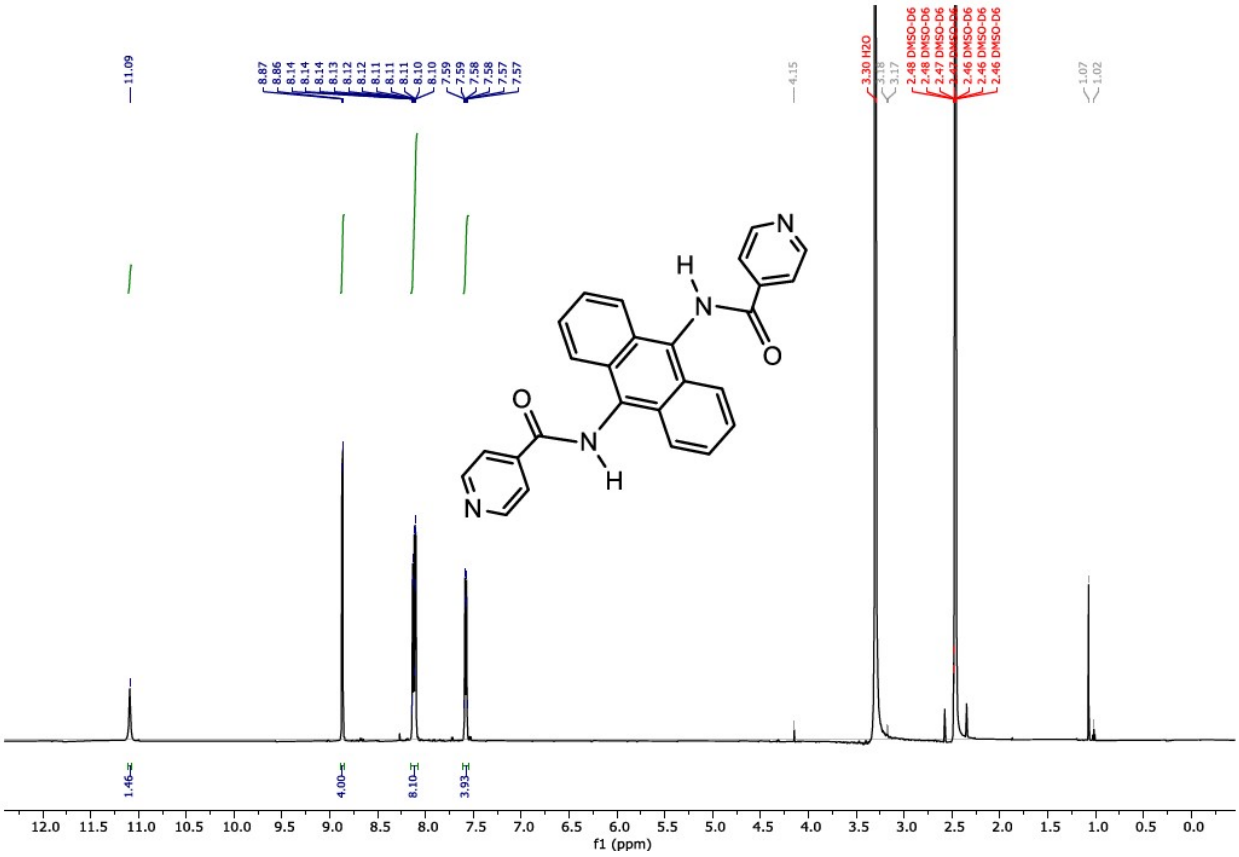


Figure S10 ^{1}H NMR spectrum of **5** (DMSO-d_6, 400 MHz, 25°C)

Mass spectra

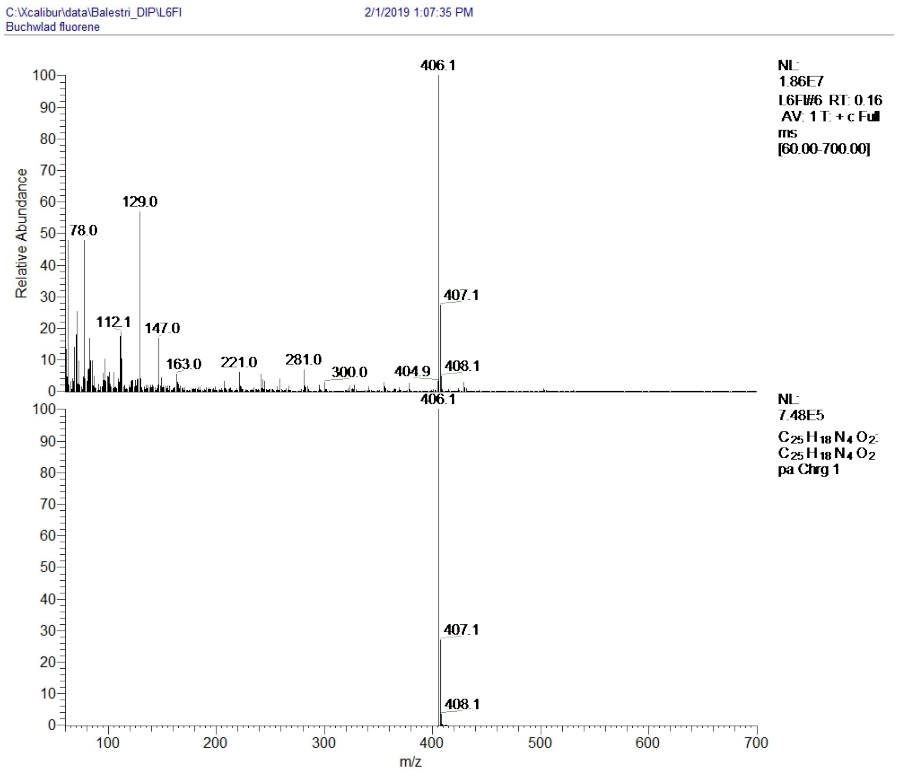


Figure S11 EI-MS(+) of spectrum of **1**

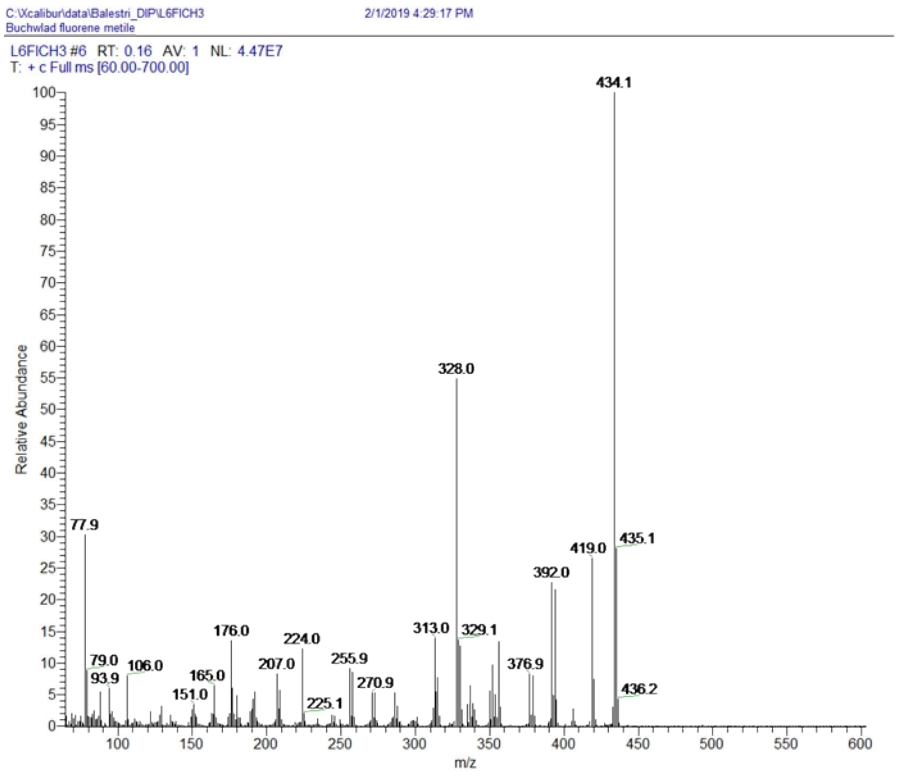


Figure S12 EI-MS(+) spectrum of **2**

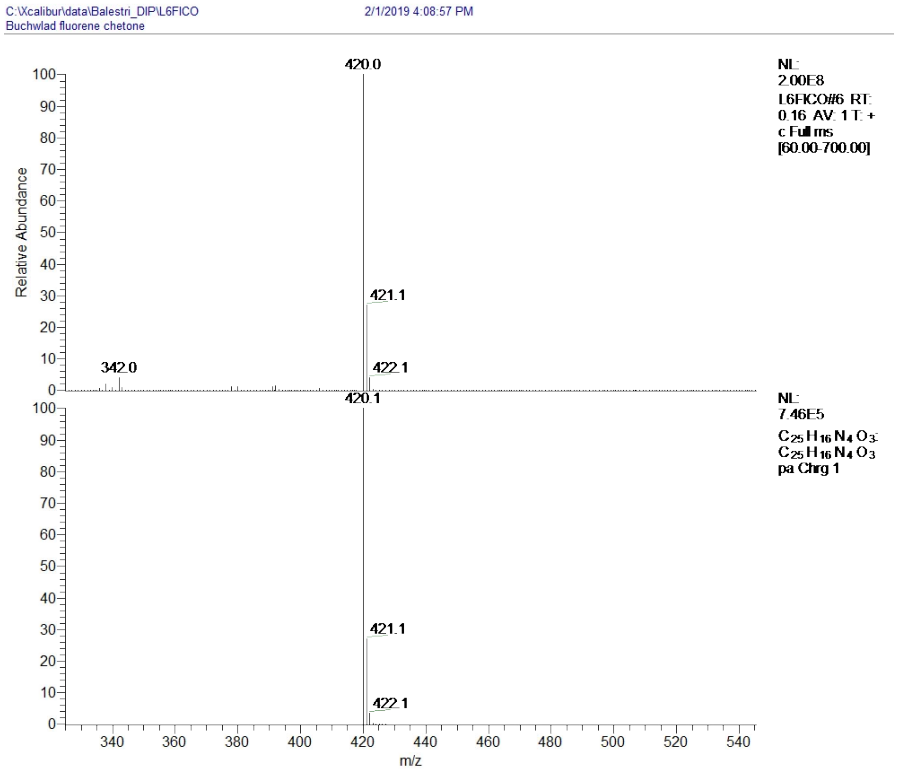


Figure S13 EI-MS(+) spectrum of **3**

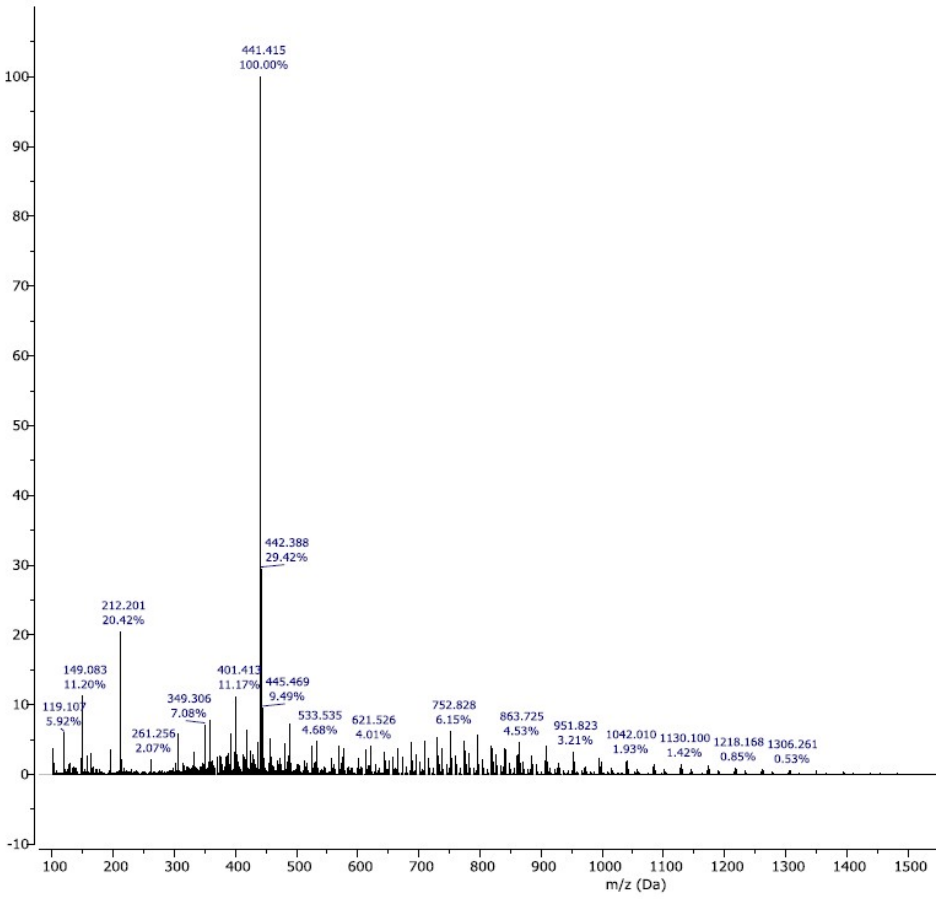


Figure S14 ESI-MS(+) spectrum of **5** (methanol, 50 V)

Crystallography

Table S1. Crystallographic data and structure refinement for **1-5**. Crystallographic data have been deposited with the CCDC 2098423-2098427 refcodes.

Identification code	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{25}H_{18}N_4O_2$	$C_{27}H_{22}N_4O_2$	$C_{25}H_{16}N_4O_3 \cdot 2H_2O$	$C_{11}H_8N_2O \cdot (C_2H_6SO)$	$C_{13}H_9N_2O \cdot (C_2H_6SO)$
Formula weight	406.43	434.48	456.45	262.32	287.35
Temperature/K	200.0	200.0	200.0	297.0	297.0
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	C2/c	P-1	P-1
a/Å	7.7678(2)	9.1477(9)	13.5492(10)	7.6003(5)	9.1303(5)
b/Å	5.82960(10)	10.3739(8)	7.4023(5)	9.7756(7)	9.5438(5)
c/Å	42.6250(9)	25.486(3)	21.4841(16)	9.7883(7)	18.2326(9)
α/°	90	89.281(5)	90	96.092(2)	86.920(2)
β/°	91.468(2)	79.975(6)	100.382(2)	103.963(2)	78.265(2)
γ/°	90	67.010(5)	90	111.340(3)	66.827(2)
Volume/Å^3	1929.56(7)	2188.4(4)	2119.5(3)	642.06(8)	1429.43(13)
Z	4	4	4	2	4
ρ_{calc}g/cm^3	1.399	1.319	1.430	1.357	1.335
μ/mm^{-1}	0.738	0.684	0.102	0.247	0.229
F(000)	848.0	912.0	952.0	276.0	604.0
Crystal size/mm^3	0.08 0.08 0.06	0.07 0.06 0.06	0.08 0.06 0.04	0.08 0.06 0.04	0.09 0.07 0.06
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.3 to 148.87	3.526 to 149.91	3.854 to 53.096	4.39 to 52.934	4.644 to 52.94
Index ranges	$-9 \le h \le 9$ $-7 \le k \le 7$ $-53 \le l \le 53$	$-10 \le h \le 11$ $-9 \le k \le 12$ $-31 \le l \le 30$	$-16 \le h \le 16$ $-9 \le k \le 8$ $-26 \le l \le 26$	$-9 \le h \le 9$ $-12 \le k \le 9$ $-12 \le l \le 12$	$-10 \le h \le 11$ $-11 \le k \le 11$ $-20 \le l \le 22$
Reflections collected	34359	24434	11535	6838	15101
Independent reflections	3947 R_{int} = 0.1363 R_{sigma} = 0.0628	7702 R_{int} = 0.1801 R_{sigma} = 0.1808	2197 R_{int} = 0.0590 R_{sigma} = 0.0482	2640 R_{int} = 0.0378 R_{sigma} = 0.0500	5819 R_{int} = 0.0357 R_{sigma} = 0.0459
Data/restraints/parameters	3947/0/280	7702/0/635	2197/0/158	2640/0/165	5819/0/365
Goodness-of-fit on F^2	1.011	0.938	1.124	1.030	0.733
Final R indexes	R_1 = 0.0585	R_1 = 0.0931	R_1 = 0.0733	R_1 = 0.0447	R_1 = 0.0545
[I>=2σ (I)]	wR_2 = 0.1410	wR_2 = 0.2102	wR_2 = 0.1461	wR_2 = 0.0947	wR_2 = 0.1699
Final R indexes	R_1 = 0.1052	R_1 = 0.2545	R_1 = 0.1008	R_1 = 0.0679	R_1 = 0.0699
[all data]	wR_2 = 0.1713	wR_2 = 0.2999	wR_2 = 0.1582	wR_2 = 0.1073	wR_2 = 0.1935
Largest diff. peak/hole / e Å^{-3}	0.21/-0.33	0.28/-0.33	0.39/-0.26	0.19/-0.24	1.10/-0.46

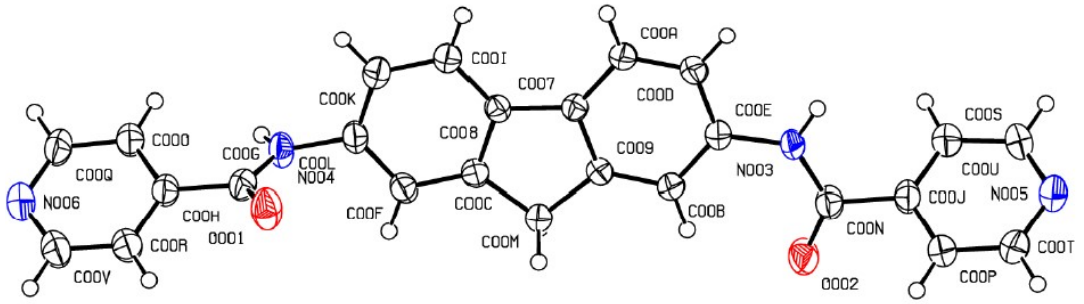


Figure S15: ORTEP drawing of **1**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity.

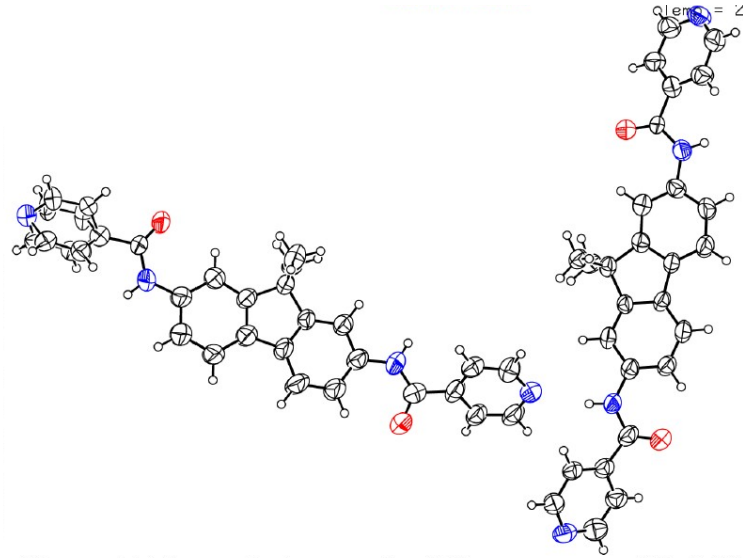


Figure S16: ORTEP drawing of **2**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style and atom labels are omitted for the sake of clarity.

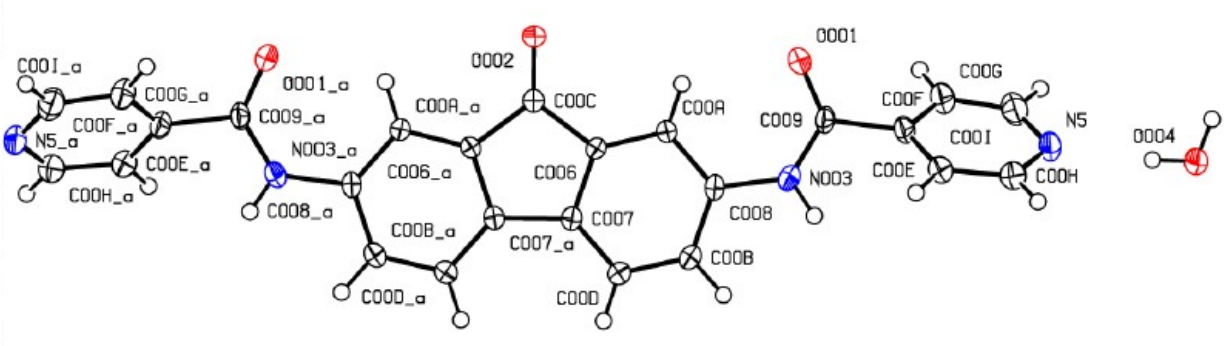


Figure S18: ORTEP drawing of **3**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity.

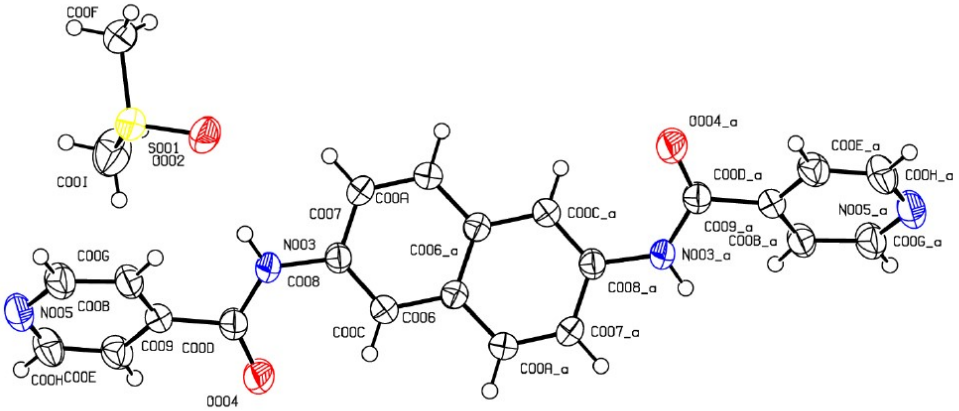


Figure S19: ORTEP drawing of **4**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity.

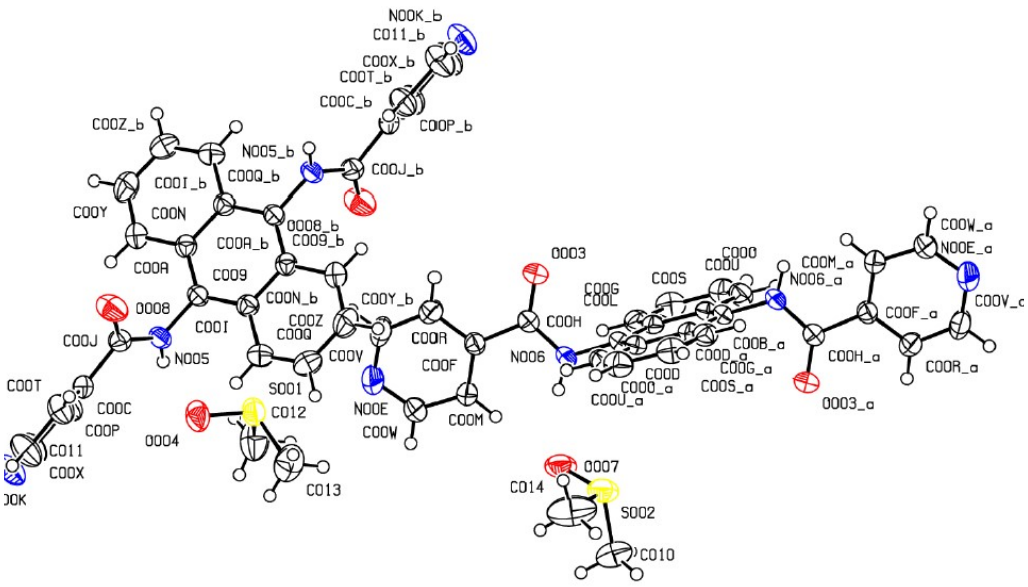


Figure S20: ORTEP drawing of **5**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity.

Spectroscopic characterization

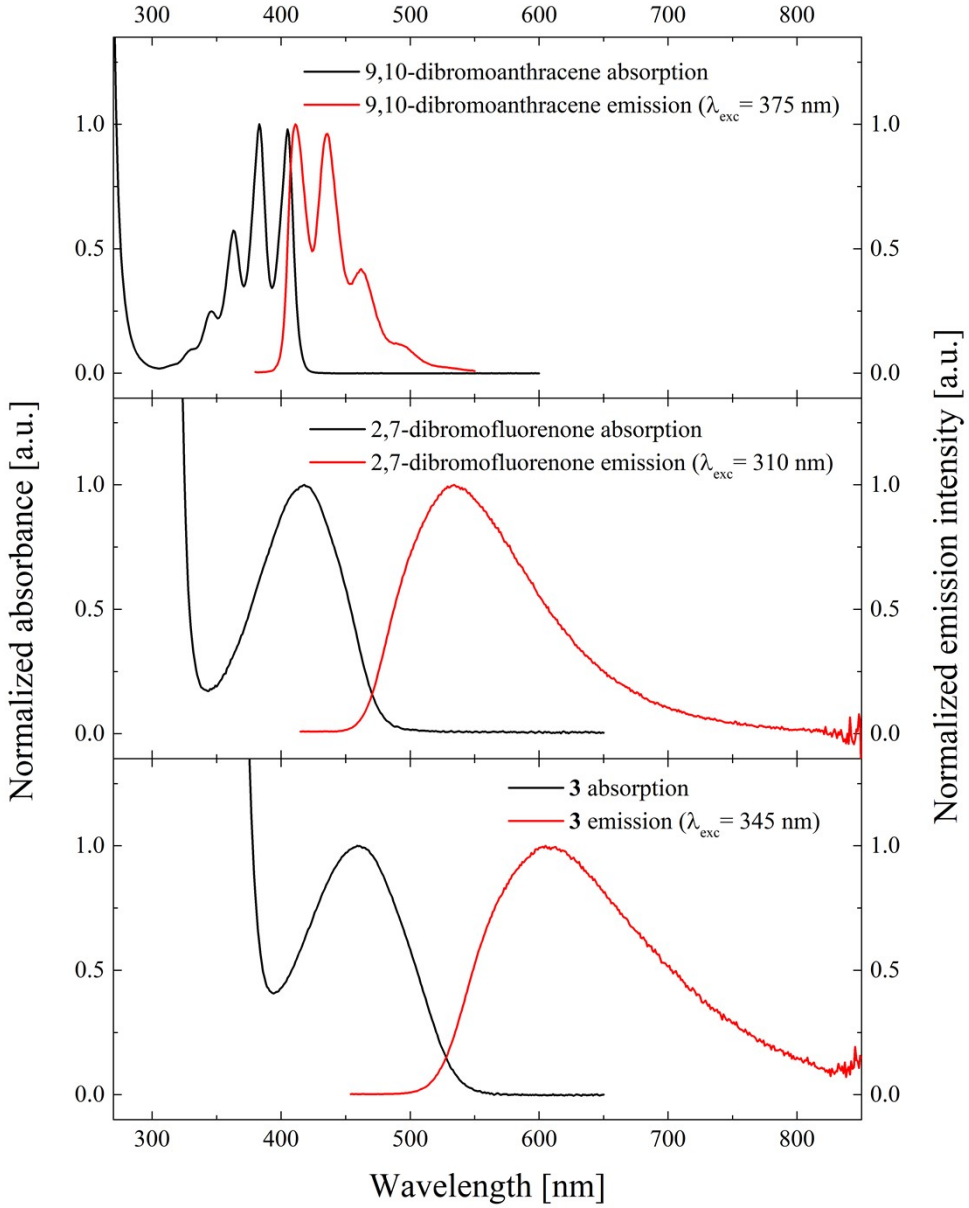


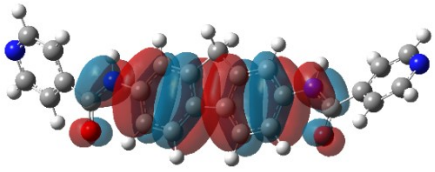
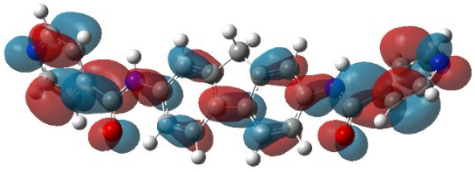
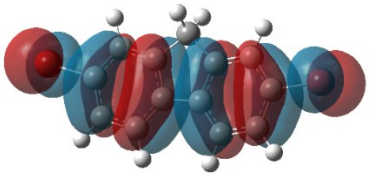
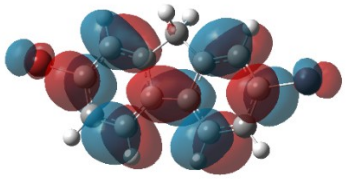
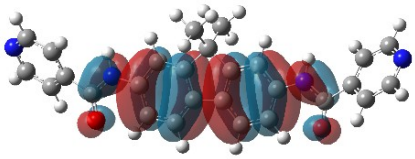
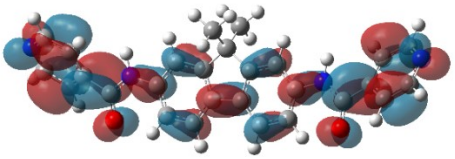
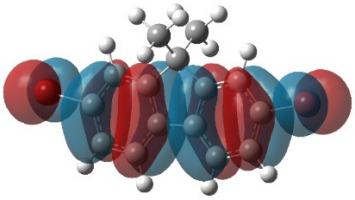
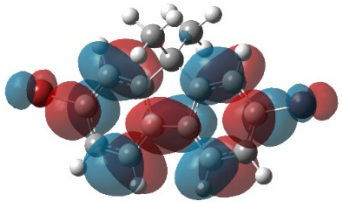
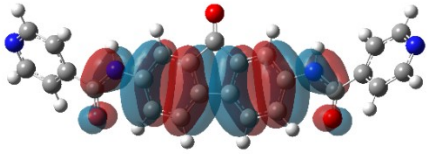
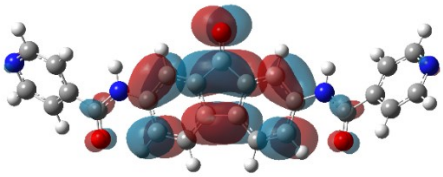
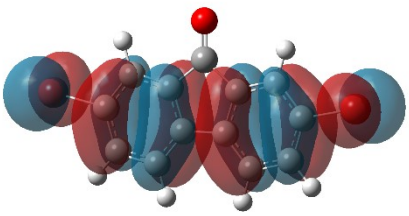
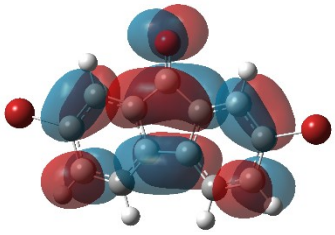
Figure S21. Absorption and emission spectra of linker **3**, 2,7-dibromofluorenone and 1,9-dibromoanthracene in DMF. The corresponding excitation and emission wavelengths are reported in the legend. Fluorescence quantum yield of **3** is <0.01 (fluorescence standard: fluorescein in NaOH 0.1M ϕ=0.9)

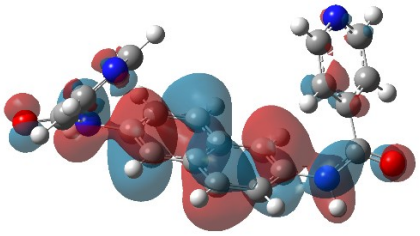
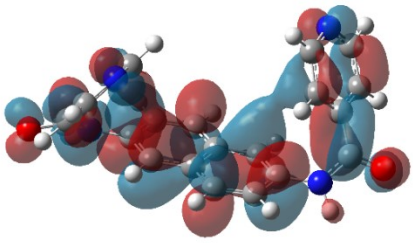
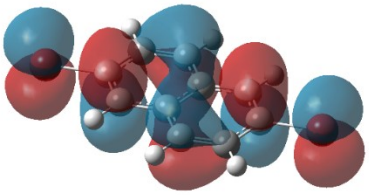
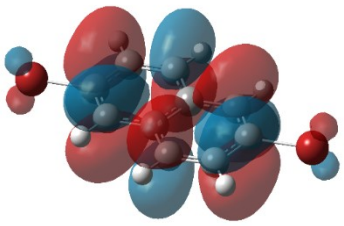
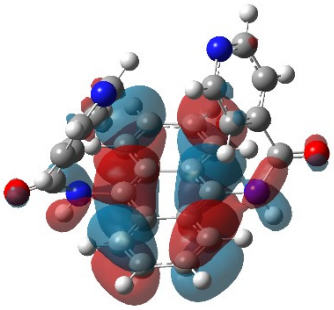
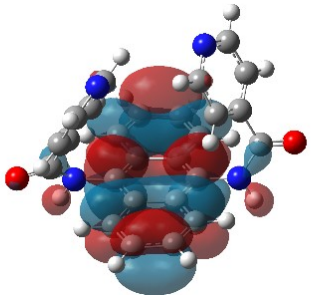
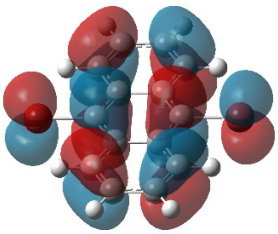
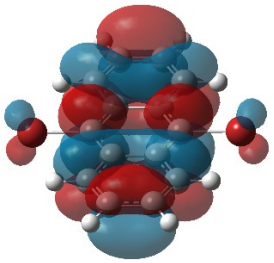
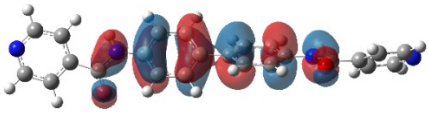
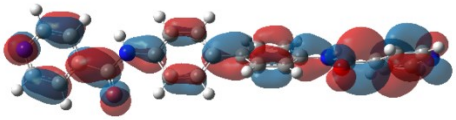
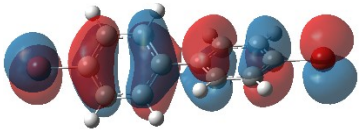
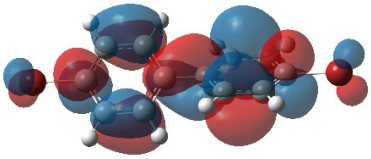
Table S2. Absorption properties in DMF of ligands **1**-**6**.

Ligand	λ_{max}^{abs} *[nm]*	*Molar extinction coefficient [$M^{-1}cm^{-1}$]*
1	338	4.80×10^4
2	340	4.50×10^4
3	344, 459	3.10×10^4, 0.158×10^4
4	330	2.13×10^4
5	375	0.979×10^4
6	322	3.31×10^4

TDDFT calculations

Table S3. HOMO/LUMO orbitals of linkers **1**-**6** and dibromo precursors.

	HOMO	LUMO
1		
2,7-dibromofluorene		
2		
2,7-dibromo-9,9-dimethyl-9H-fluorene		
3		
2,7-dibromo-9-fluorenone		

4		
2,6-dibromonaphthalene		
5		
9,10-dibromoanthracene		
6		
4,4'-dibromobiphenylene		

In order to inquire if multiple configurations are accessible at room temperature, a relaxed scan on the ground state potential energy surface of linker **6** has been performed, scanning over the two amide bonds dihedral angles using M062X as functional and 6-31G(d,p) as basis set.

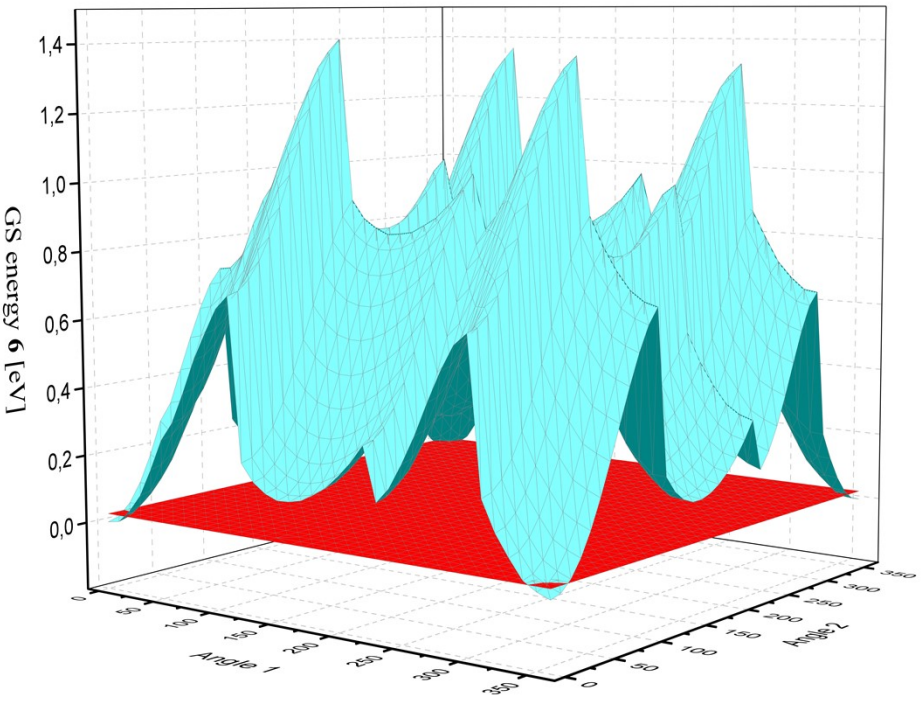


Figure S22. Ground state energy of linker **6** as a function of the two amide bonds dihedral angles. The red plane denotes the thermal energy at room temperature (0.025 eV).

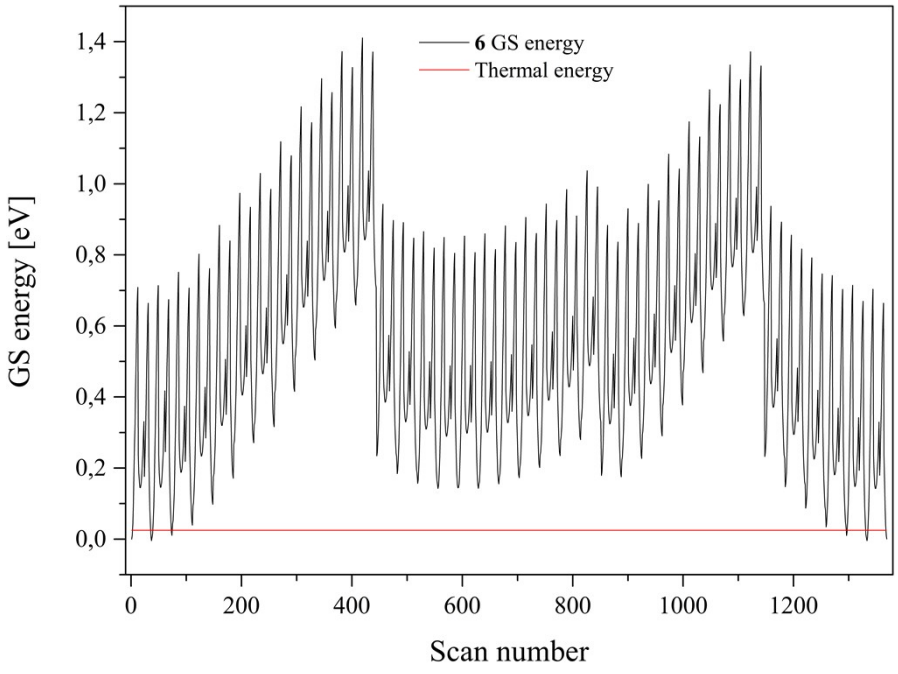
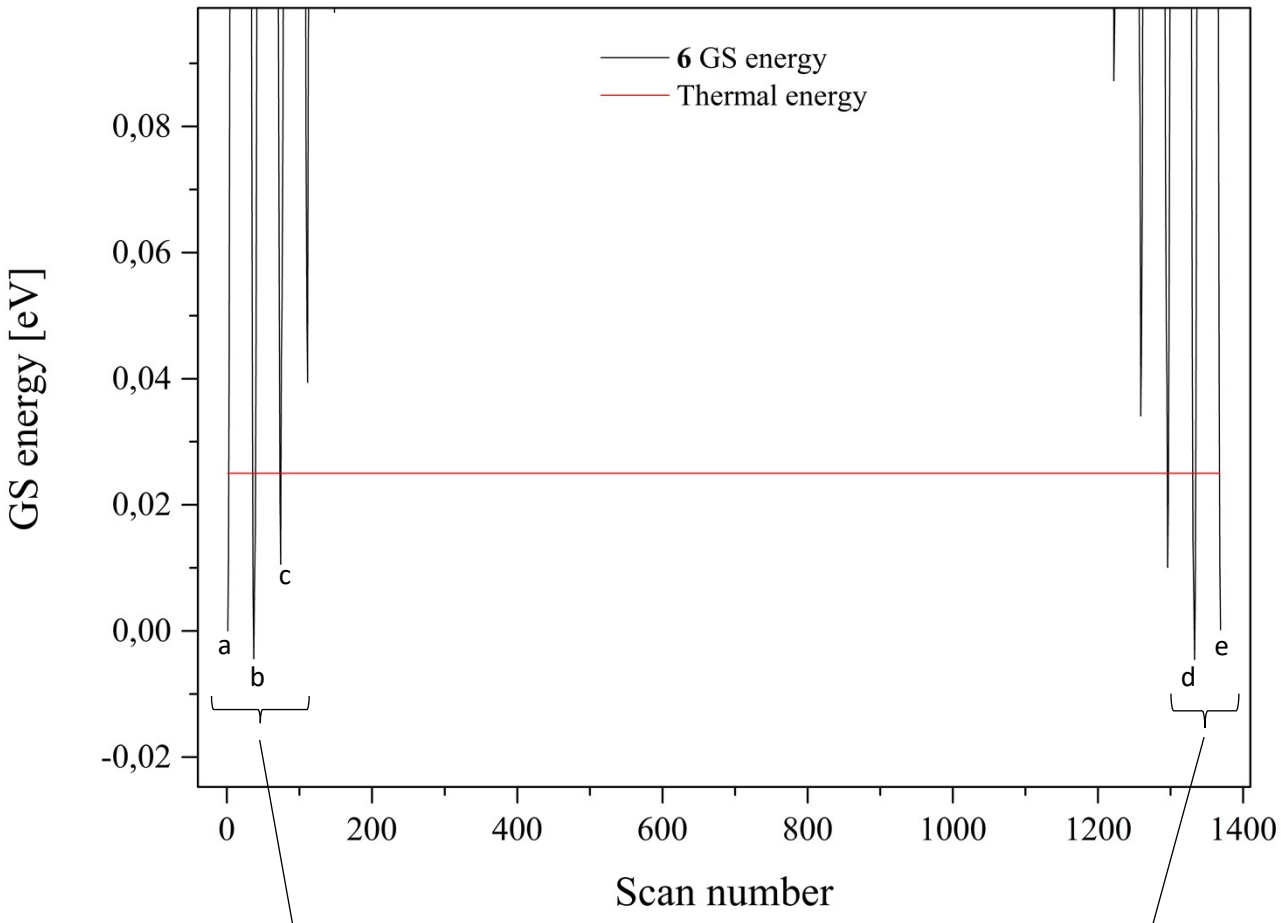
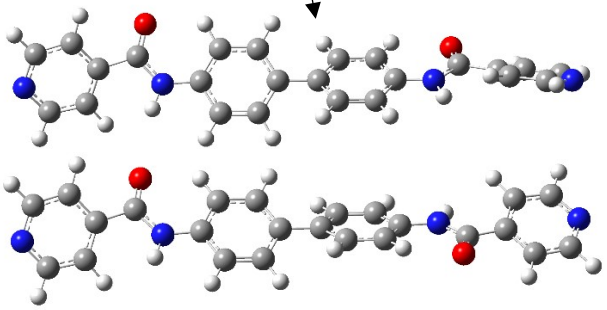


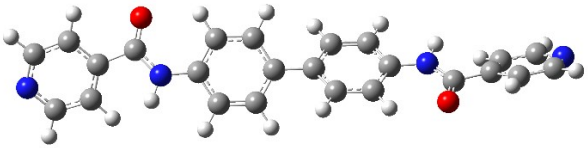
Figure S23. Ground state energy of linker **6** as a function of the scan number. In correspondence of each scan step, one of the two angles has been increased by 10 degrees, in order to make a complete rotation for both.


6 GS energy
Thermal energy
GS energy [eV]
0,08
0,06
0,04
0,02
0,00
-0,02
0
200
400
600
800
1000
1200
1400
Scan number
a
b
c
d
e

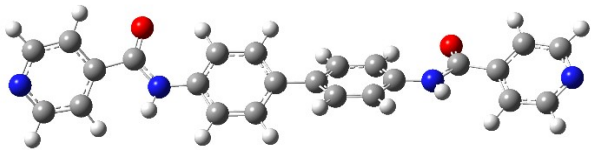
a.



b.



c.



d.

e.

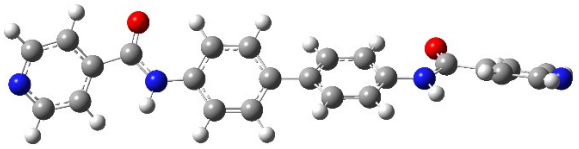


Figure S24. Above: enlargement of Figure S23; Below: linker **6** conformations characterized by lower energy than the thermal energy at room temperature.

Table S4. TDDFT results for ligand 4 in gas phase. The results for the first and second excited states are reported.

Excited state	*Transition energy [eV]*	*Oscillator strength*	*Main orbital contributions*	
1	4.24	0.03	HOMO → LUMO HOMO → LUMO+1	(0.44) (-0.44)
2	4.41	0.16	HOMO → LUMO HOMO → LUMO+1	(0.47) (0.33)