Supporting Information

Biscoumarin-containing Acenes as Stable Organic Semiconductors for Photocatalytic Oxygen Reduction to Hydrogen Peroxide

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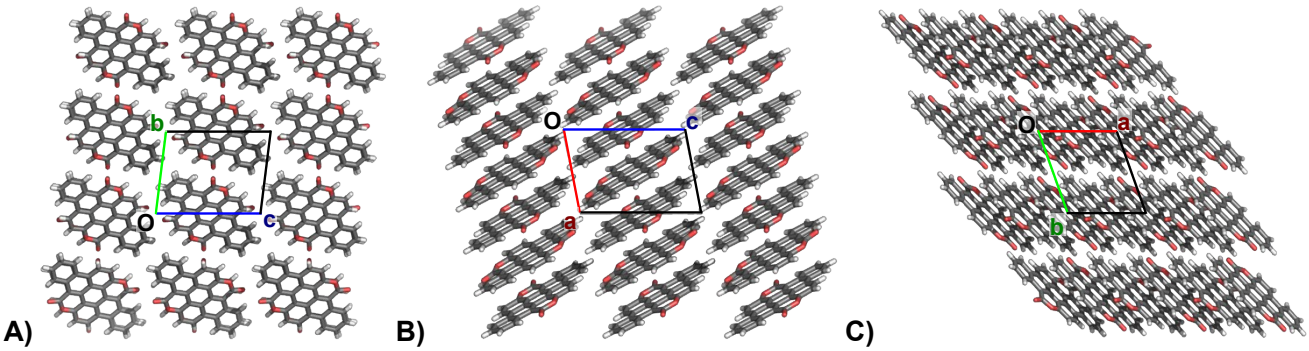
X-ray diffraction

Data collections were performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron, Trieste (Italy)[1S]. Complete datasets were collected at 100 K (nitrogen stream supplied through an Oxford Cryostream 700) with a monochromatic wavelength of 0.700 Å through the rotating crystal method. Images were acquired using a Pilatus 2M image plate detector. The crystals of compounds **8**, **9** and **10** were dipped in N-paratone and mounted on the goniometer head with a nylon loop. The diffraction data were indexed, integrated and scaled using XDS.[2S] **8** and **10** crystallize with triclinic *P* -1 unit cells. Complete dataset was obtained by merging two data collections obtained from two different orientations of two different crystals. **9** crystallizes with a monoclinic *P* $2_1/c$ unit cell. The unit cell and space group have also been determined at room temperature and no phase change has been detected for the three compounds. The structures were solved by direct methods using SIR2014,[3S] Fourier analyzed and refined by the full-matrix least-squares based on F^2 implemented in SHELXL-2014.[4S] The Coot program was used for modeling.[5S] Anisotropic thermal motion modeling was then applied to atoms with full occupancy. Hydrogen atoms were included at calculated positions with isotropic $U_{factors} = 1.2\ U_{eq}$.

All the molecules show an inversion center that matches crystallographic inversion centers. The asymmetric units contain two crystallographically half independent moieties for **8** and **9** and one plus half molecules for **10**. No disorder and no solvent molecules are present in these crystals forms. Essential crystal and refinement data (Table S1) are reported below.



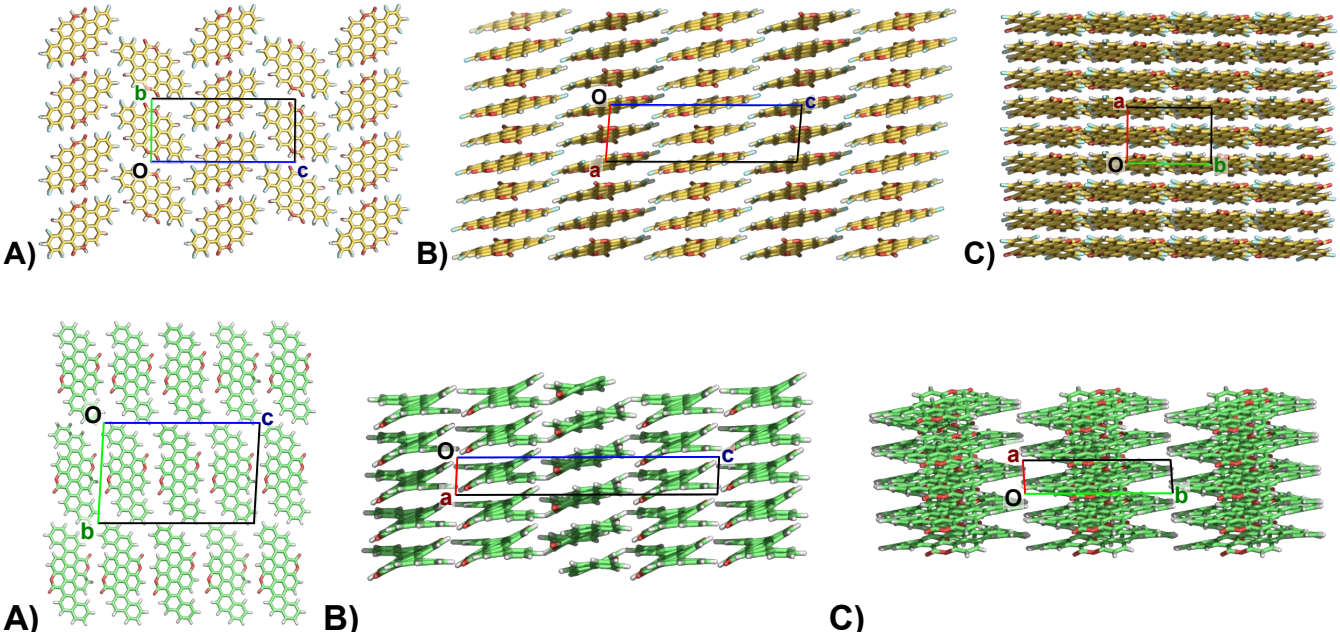


Fig. S1. Crystal packing of **8**, **9**, and **10** (from top to bottom)

Table S1. Crystallographic data and refinement details for compounds **8-10.**

	8 at 100K	**8** at 298K	**9** at 100K	**9** at 298K	**10** at 100K	**10** at 298K
CCDC Number	1531580	1531579	1531582	1531584	1531581	1531583
Moiety Formula	$C_{30}H_{12}O_4$	$C_{30}H_{12}O_4$	$C_{30}H_8F_4O_4$	$C_{30}H_8F_4O_4$	$C_{38}H_{16}O_4$	$C_{38}H_{16}O_4$
Empirical Formula	$C_{30}H_{12}O_4$	$C_{30}H_{12}O_4$	$C_{30}H_8F_4O_4$	$C_{30}H_8F_4O_4$	$C_{38}H_{16}O_4$	$C_{38}H_{16}O_4$
Formula weight (Da)	436.40	436.40	508.36	508.36	536.51	536.51
Temperature (K)	100(2)	298(2)	100(2)	298(2)	100(2)	298(2)
Wavelength (Å)	0.700	0.700	0.700	0.700	0.700	0.700
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space Group	*P*-1	*P*-1	$P2_1/c$	$P2_1/c$	*P*-1	*P*-1
a (Å)	8.910(2)	9.009(2)	7.239(1)	7.334(2)	3.798(1)	3.839(1)
b (Å)	9.404(2)	9.437(2)	10.792(2)	10.849(2)	16.829(3)	16.867(3)
c (Å)	11.968(2)	12.056(2)	24.598(5)	24.774(5)	26.367(5)	26.618(5)
α (°)	77.86(3)	77.63(3)	90	90	92.78(3)	92.87(3)
β (°)	74.36(3)	74.11(3)	94.27(3)	92.14(3)	92.17(3)	91.46(3)
γ (°)	67.64(3)	68.35(3)	90	90	93.76(3)	93.89(3)
V (Å^3)	886.5(4)	908.9(4)	1916.3(7)	1969.8(7)	1678.3(6)	1716.7(6)
Z	2	2	4	4	3	3
ρ (g·cm^{-3})	1.635	1.595	1.762	1.714	1.593	1.557
F(000)	448	448	1024	1024	828	828
μ (mm^{-1})	0.104	0.101	0.136	0.133	0.099	0.099
θ min,max (°)	2.3, 27.4	1.7, 24.0	1.6, 26.7	1.6, 27.4	0.8, 28.2	0.8, 29.1
Resolution (Å)	0.76	0.86	0.78	0.76	0.74	0.72
Total refl. collctd	33081	12898	21123	29801	39146	49313
Independent refl.	4174 [R(int) = 0.0736]	2881 [R(int) = 0.1392]	4172 [R(int) = 0.0483]	4597 [R(int) = 0.0641]	8429 [R(int) = 0.0696]	9424 [R(int) = 0.0312]
Obs. Refl. [Fo>4σ(Fo)]	2880	1792	2544	2435	7734	7656
I/σ(I) (all data)	10.42	4.14	10.35	7.25	13.25	19.6

I/σ(I) (max resltn)	6.13	2.29	4.11	2.45	11.27	10.6
Completeness (all data)	0.99	0.97	0.99	0.97	0.98	0.98
Completeness (max resltn)	0.99	0.95	0.95	0.95	0.98	0.95
Rmerge (all data)	0.107	0.083	0.066	0.100	0.046	0.089
Rmerge (max resltn,)	0.233	0.248	0.323	0.368	0.053	0.042
Multiplicity (all data)	7.9	4.3	5.1	6.2	4.6	5.1
Multiplicity (max resltn)	6.7	3.9	4.5	6.0	4.2	4.8
Data/restraint/parameters	4174/0/308	2881/0/308	4172/0/344	4597/0/344	8429/0/569	9424/0/569
Goof	1.016	1.016	1.017	1.006	1.050	1.036
$R_1{}^a$ [I>2.0σ(I)], $wR_2{}^a$ [I>2.0σ(I)]	0.0662, 0.1734	0.0596, 0.1479	0.0537, 0.1373	0.0599, 0.1481	0.0662, 0.1780	0.0583, 0.1618
$R_1{}^a$ (all data), $wR_2{}^a$ (all data)	0.0937, 0.2007	0.0957, 0.1778	0.0949, 0.1637	0.1081, 0.1835	0.0693, 0.1811	0.0683, 0.1708

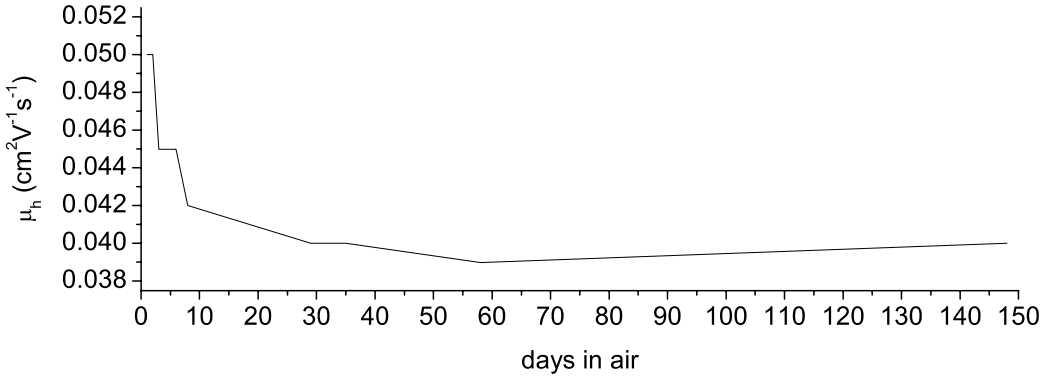


Fig. S2. Hole mobility of **10** in thin film transistor geometry over 150 days of measurement.

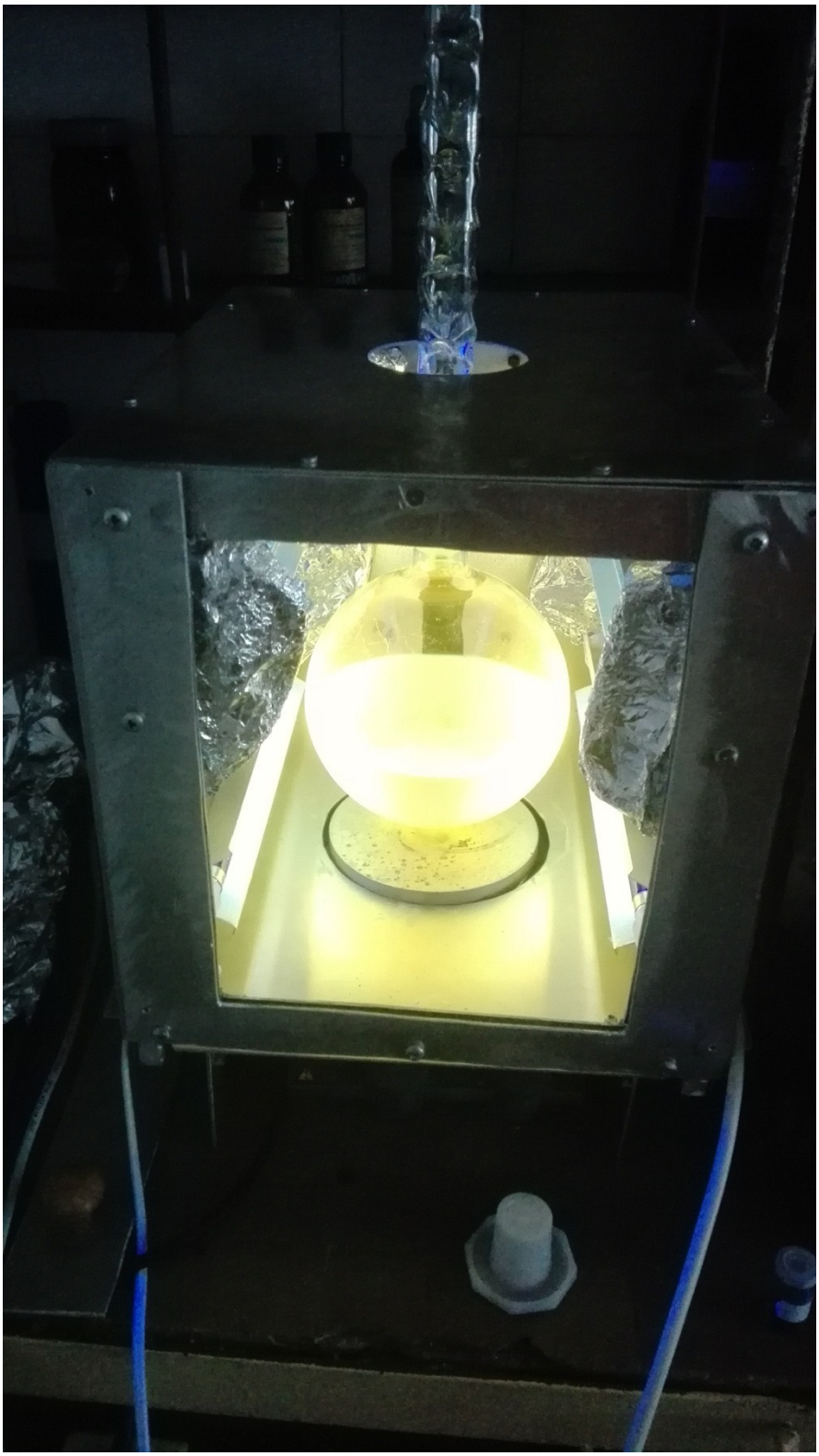


Fig. S3. Photo of the photoreactor (365 nm) used in this project.

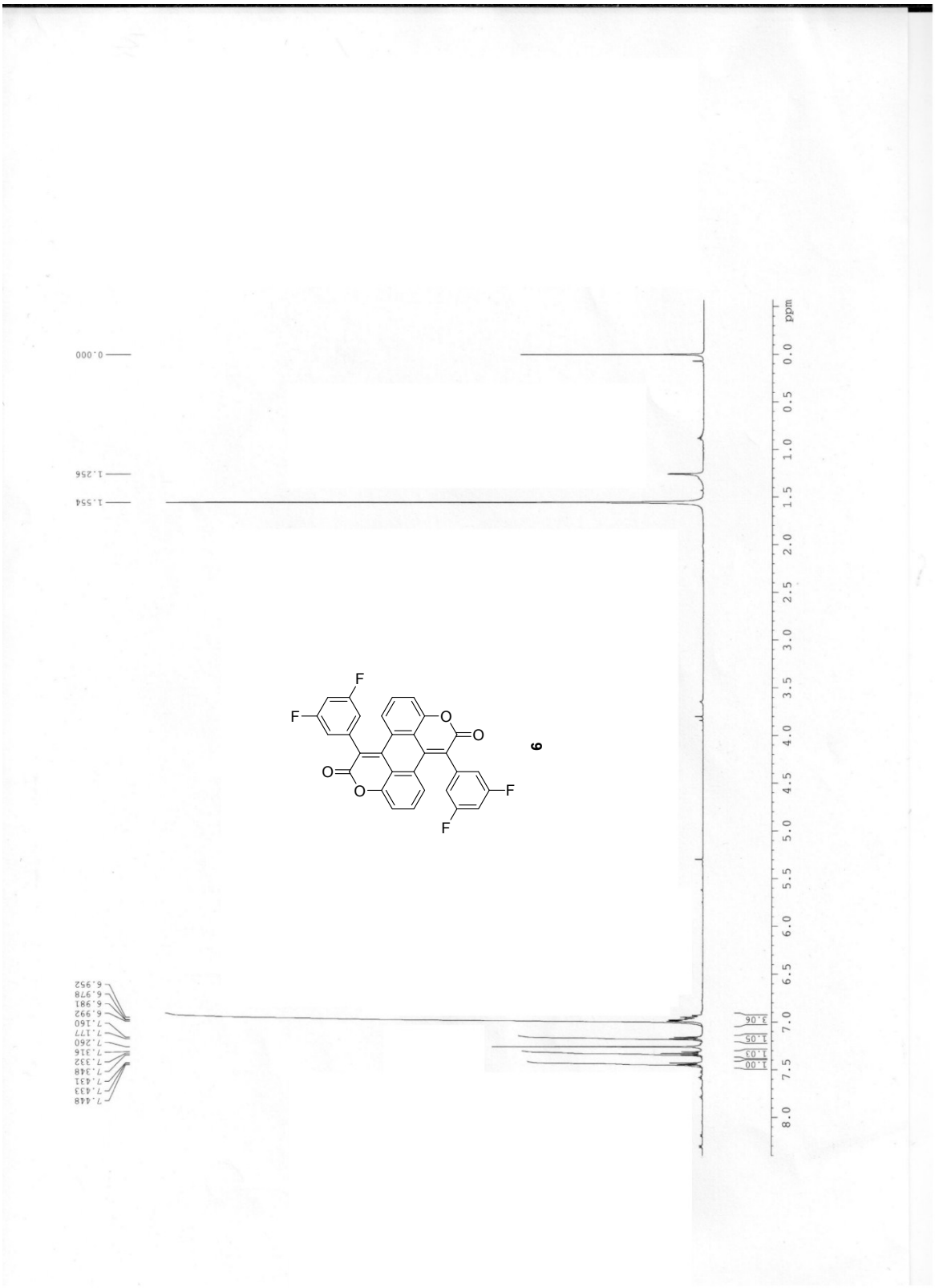


Fig. S4. ^{1}H NMR (500 MHz) spectrum of compound **6**.

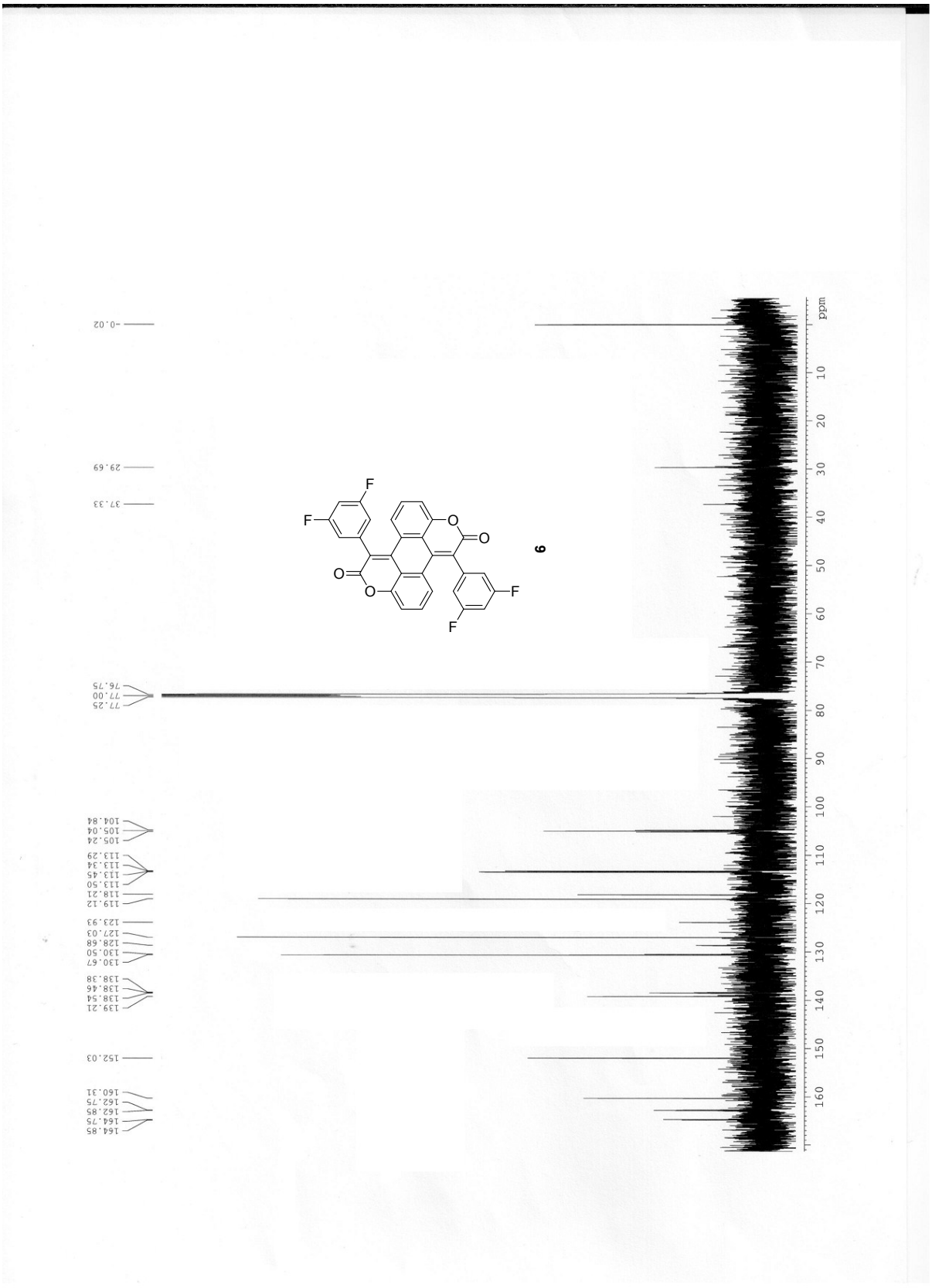


Fig. S5. ^{13}C NMR (151 MHz)spectrum of compound **6**.

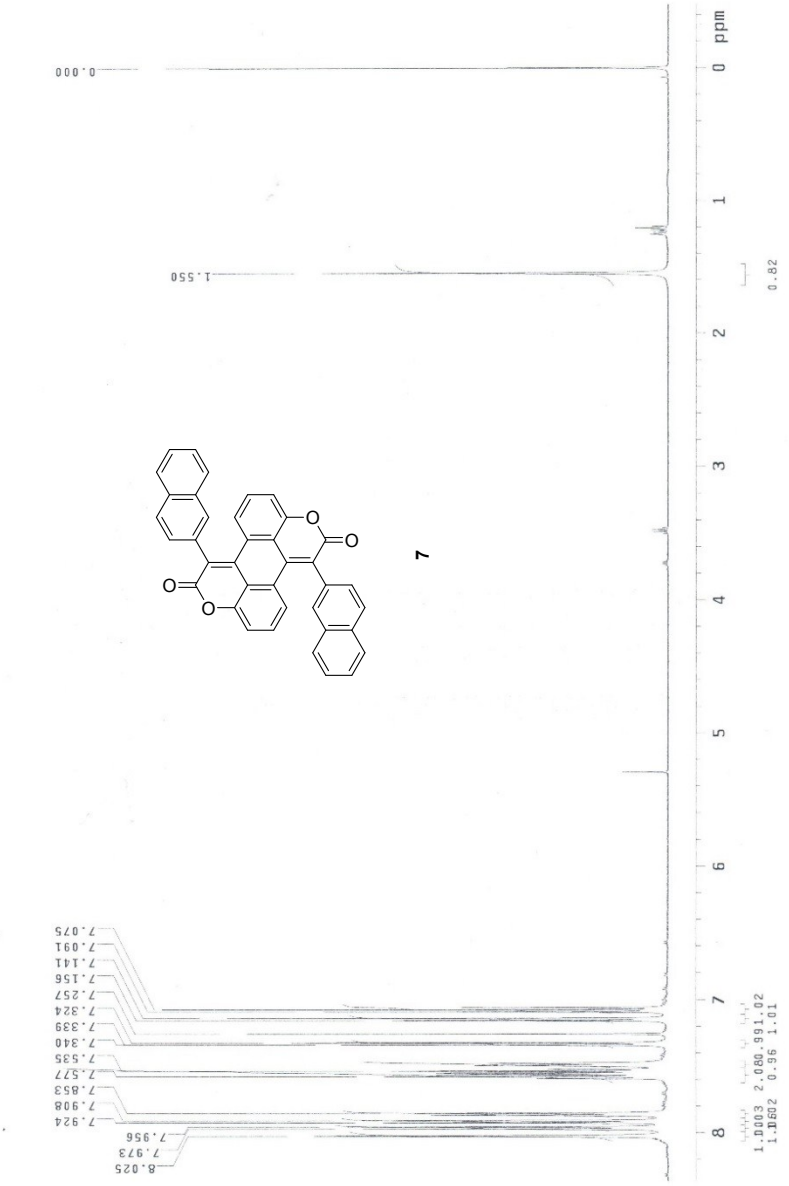


Fig. S6. [1]H NMR (500 MHz) spectrum of compound **7**.

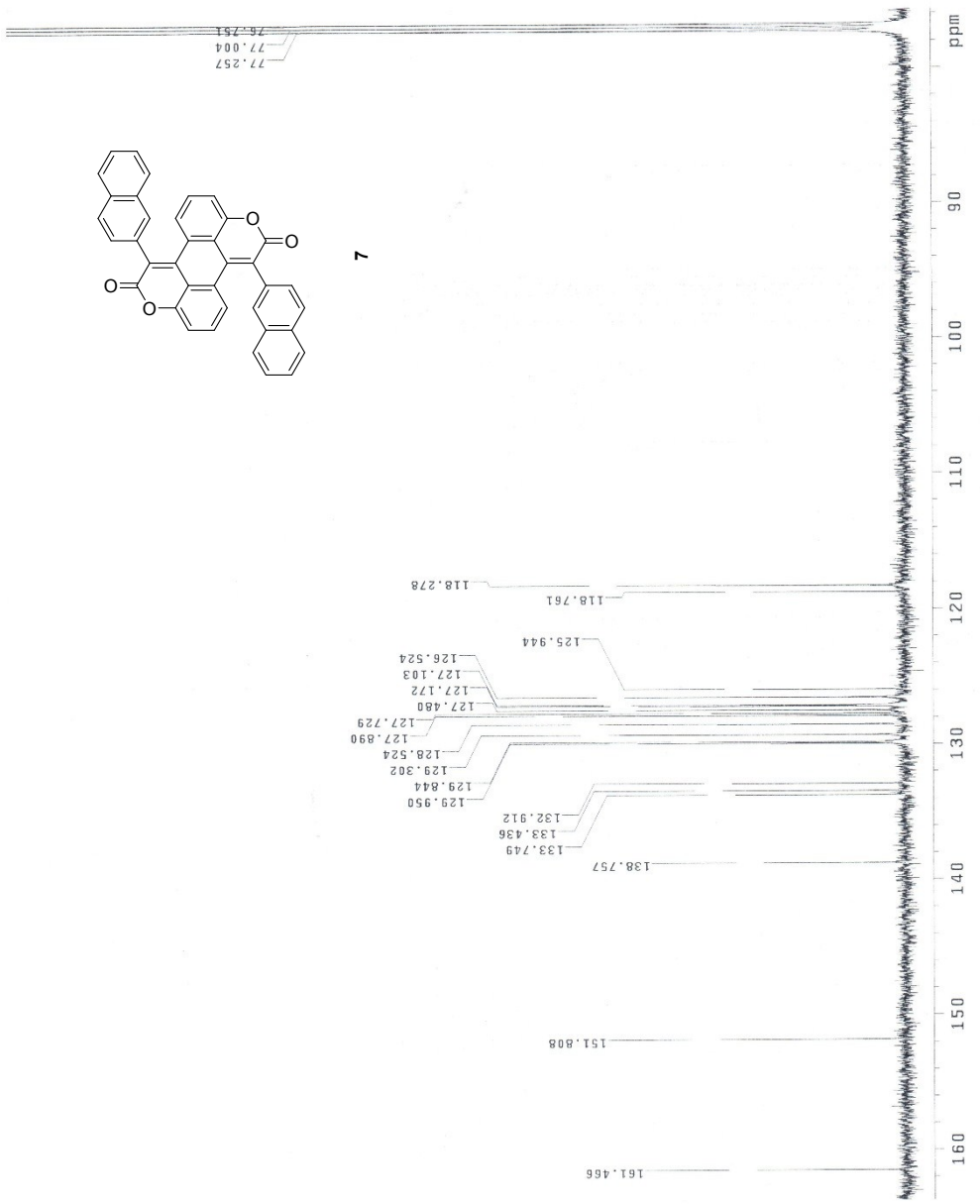


Fig. S7. ^{13}C NMR (151 MHz)spectrum of compound **7**.

References

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