1, 4, 8, 11, 15, 18, 22, 25-Alkylsulfanyl phthalocyanines. Effect of macrocycle distortion on packing and spectroscopic properties

Supporting information

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Content

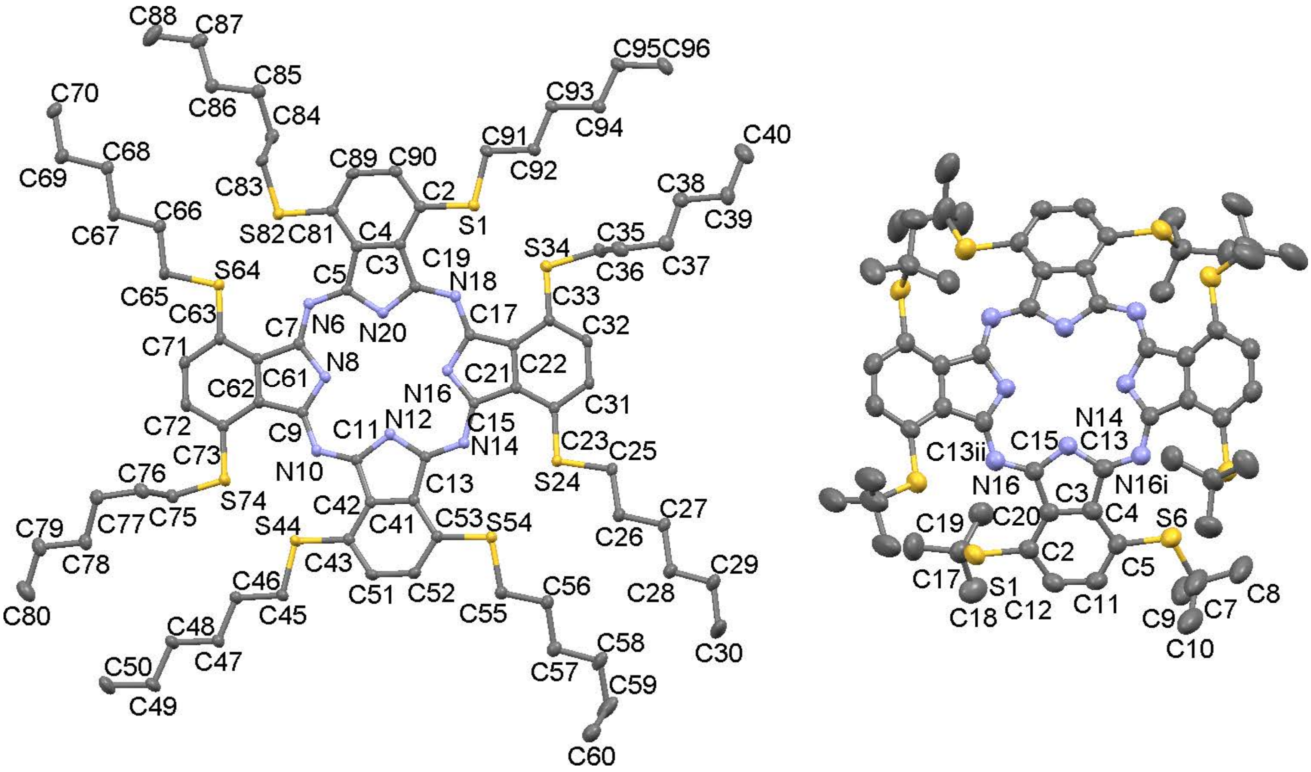


Fig. S1 Atom numbering scheme for phthalocyanine **1** (left) and phthalocyanine **2** (right)

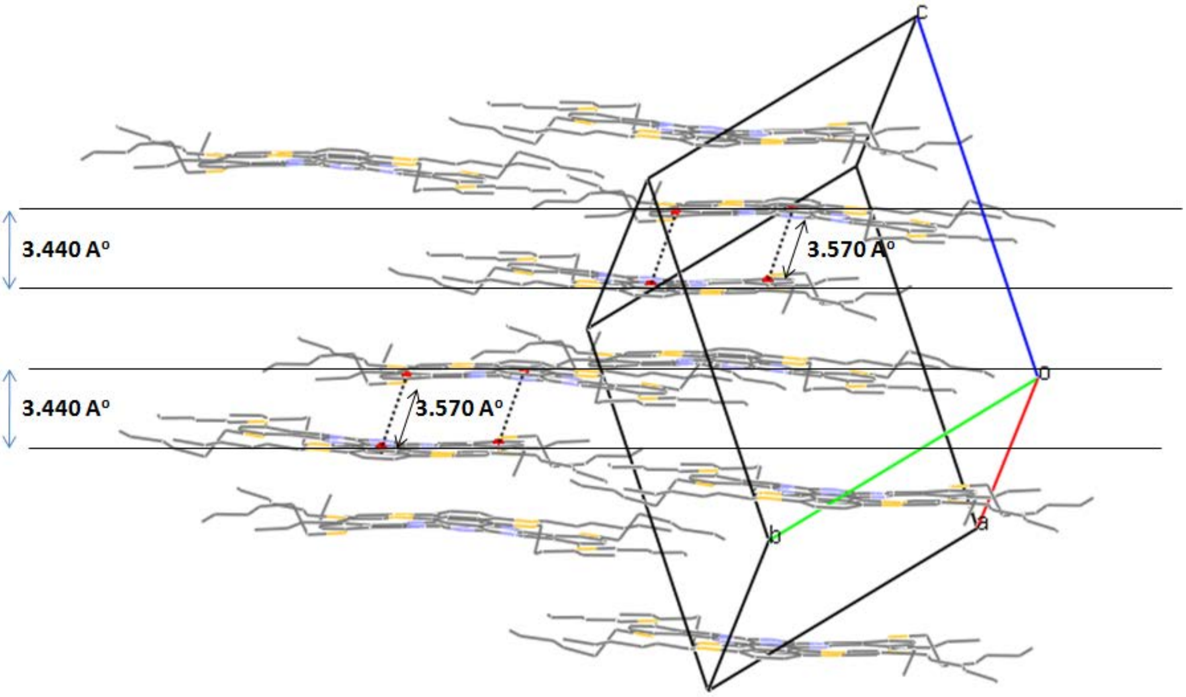


Fig. S2 Packing of phthalocyanine **1** showing the shortest π-π stacking interaction (3.570 Å) in the unite cell.

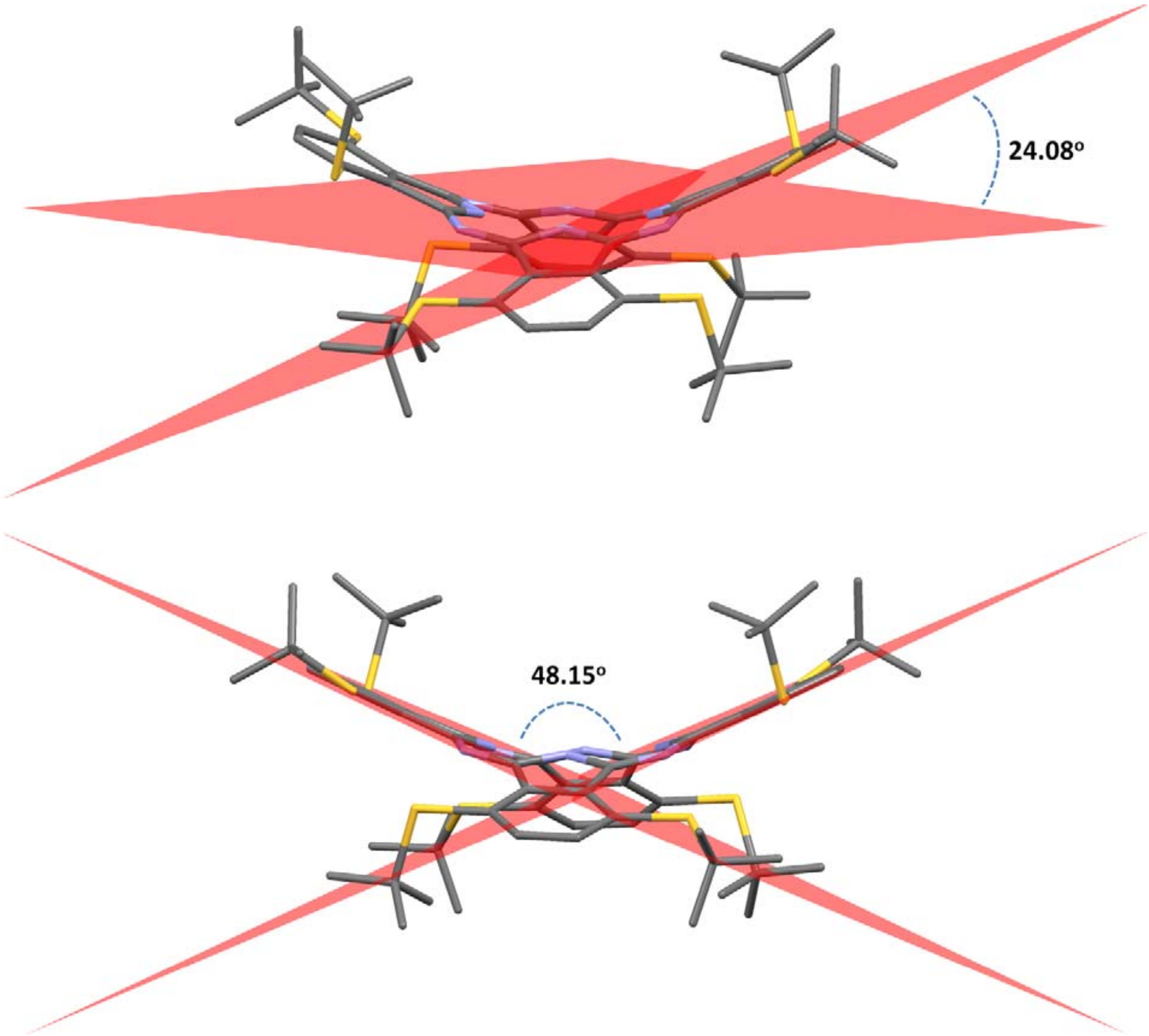


Fig. S3 Top: perspective view of **2** showing the deviations of the isoindole rings from the 4N mean plane. Bottom: perspective view of **2** showing the dihedral angle between the pair of the planes generated by the isoindole unites.

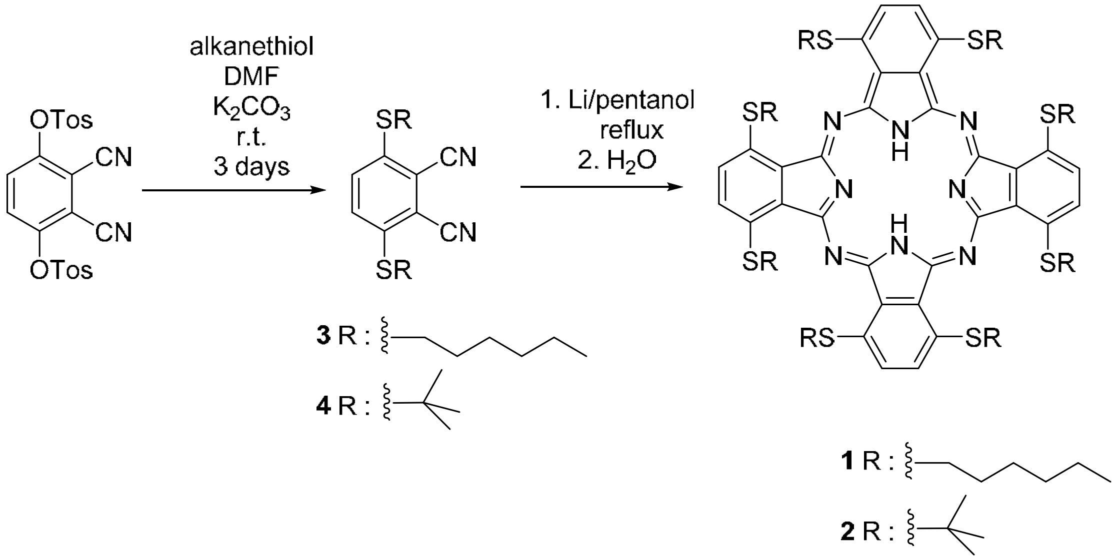
Synthesis and characterization

Materials and methods

Solvents and chemicals were purchased from Aldrich or Alfa Aesar and used as received. Mass spectra were recorded on a MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as the matrix. High resolution mass spectra were recorded on a BRUKER MicroTOFQ-II with an ESI (electrospray ionization) ion source in positive mode. The sample was infused at 150 µL/h in 50:50 water and acetonitrile with 0.1% of formic acid. The gas flow of the sprayer is 0.6 bar, and the spray voltage is 3.5 kV. The capillary temperature is 200 °C. The ions are transferred to the TOF by using mild conditions on ion optics (the two ion funnels, the hexapole, the quadrupole, and the collision cell) to preserve the complex. The mass range of the TOF is 50−5000 m/z and the calibration was done with cesium iodide. Melting points were recorded on a Stuart device. IR spectrum was recorded between 4000 and 650 cm^{-1} using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. Electronic absorption spectra in the UV-visible region were recorded with a Shimadzu 2001 UV spectrophotometer using a 1 cm path length cuvette at room temperature. The HPLC system is a Agilent 1100 series HPLC system (ChemStation software) equipped with a G 1311A pump and G1315B diode array detector monitoring the range 254–900 nm. Use of a normal phase column Lichrosorb-SI-60 (250 x 4.6 mm) from Alltech. Assocciates, Inc. The purity of **1** and **2** have been checked by normal phase HPLC. The mobile phase was a 98/2 (v/v) mixture of chloroform–THF. The flow-rate was set at 1 $ml.min^{-1}$ and the samples were dissolved in chloroform at a concentration 1 $mg.ml^{-1}$ for the normal phase. Under these conditions, the retention time for **1** and **2** were found to be 3.16 and 2.75 min., respectively. 3,6-di-*tert*-Butylsulfanylphthalonitrile [1] and 3,6-dihexylsulfanylphthalonitrile [2] were prepared following literature reports from corresponding ditosylated 3,6-dicyanohydroquinone.[3]

General protocol for the preparation of phthalocyanines

Phthalocyanines **1** and **2** were prepared by previously reported lithium-assisted templating method [4] from the corresponding phthalonitriles (Scheme S1).



Scheme S1 Preparation of phthalocyanines **1** and **2**

Phthalonitriles were dissolved in pentanol at 60°C, lithium granules were added and the reaction mixture was refluxed. The colour change of the reaction mixture to green was observed concomitantly to a degagement of hydrogen gas indicating the formation of lithium pentanolate. After cooling down, the reaction mixture are poured in a 50:50 mixture of ethanol:water. The resulting precipitated phthalocyanine is filtrated and purified on a silica gel coloum chromatography. Difficulties were encountered during the preparation of **2** which quickly decomposes. Therefore the reaction is interrupted 30 minutes after the first observation of a green colour, eventhough starting phthalonitrile is recovered. Attempts to last longer the reaction lead most of the times to the degradation of the expected phthalocyanine.

Preparation of phthalocyanine 1

Reaction was initiated from phthalonitrile **3** (3.3 g, 10 mmol) and yielded 1.51 g of a dark purple brown solid (42 %). $C_{80}H_{114}N_8S_8$, MW 1444.33. m.p. 175-180°C (dec). MS (MALDI-TOF) *m/z* 1445.54 [MH+]. ATR-IR (ν, cm^{-1}) 3297, 2952, 2921, 2851, 1561, 1460, 1432, 1366, 1310, 1270, 1224, 1158, 142, 1090, 1028, 907, 867, 788, 753, 723, 708. HRMS *m/z* (experimental) 1443.6997; $C_{80}H_{115}N_8S_8$ *m/z* (theoretical) 1443.7005. Error: 0.6 ppm. HPLC t_R (min) 3.16. UV-Vis λmax nm (log ε) in THF: 805 (5.16), 720 (4.58), 350 (4.68), in $CHCl_3$: 810 (5.18), 720 (4.59), 350 (4.70)

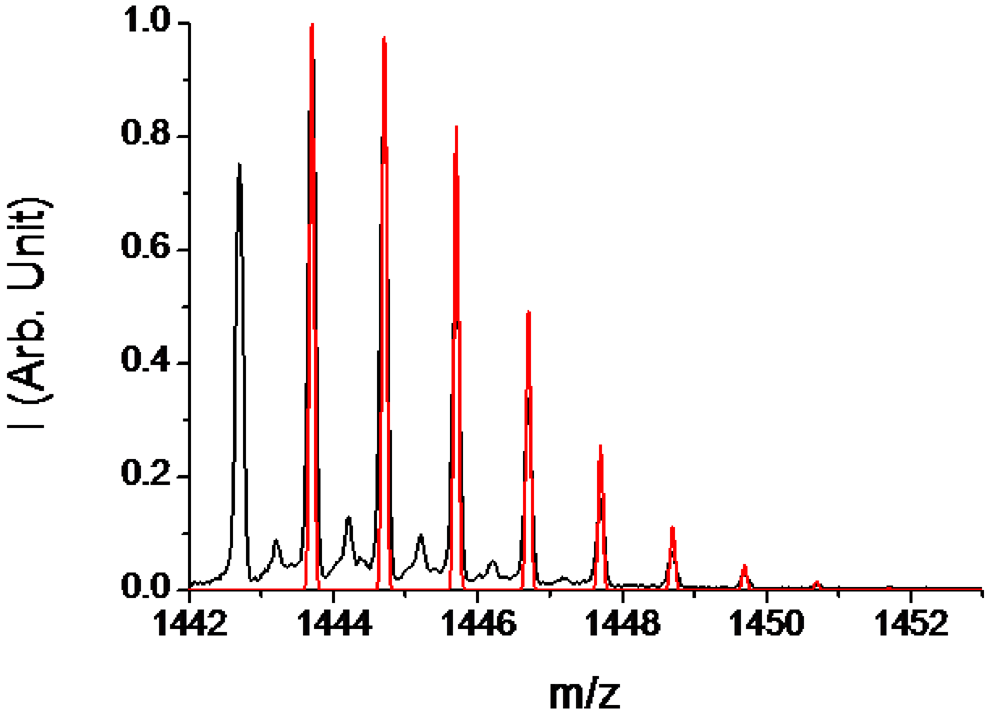


Fig. S4 High resolution mass spectrum (ESI-TOF) of compound **1**. Theoretical (red) and experimental (black) isotopic patterns. m/z (experimental) = 1443.6997; $C_{80}H_{115}N_8S_8$ m/z (theoretical) 1443.7005. Error: 0.6 ppm. The observed molecular ions in ESI are a mixture of M+ and $[M+H]^+$

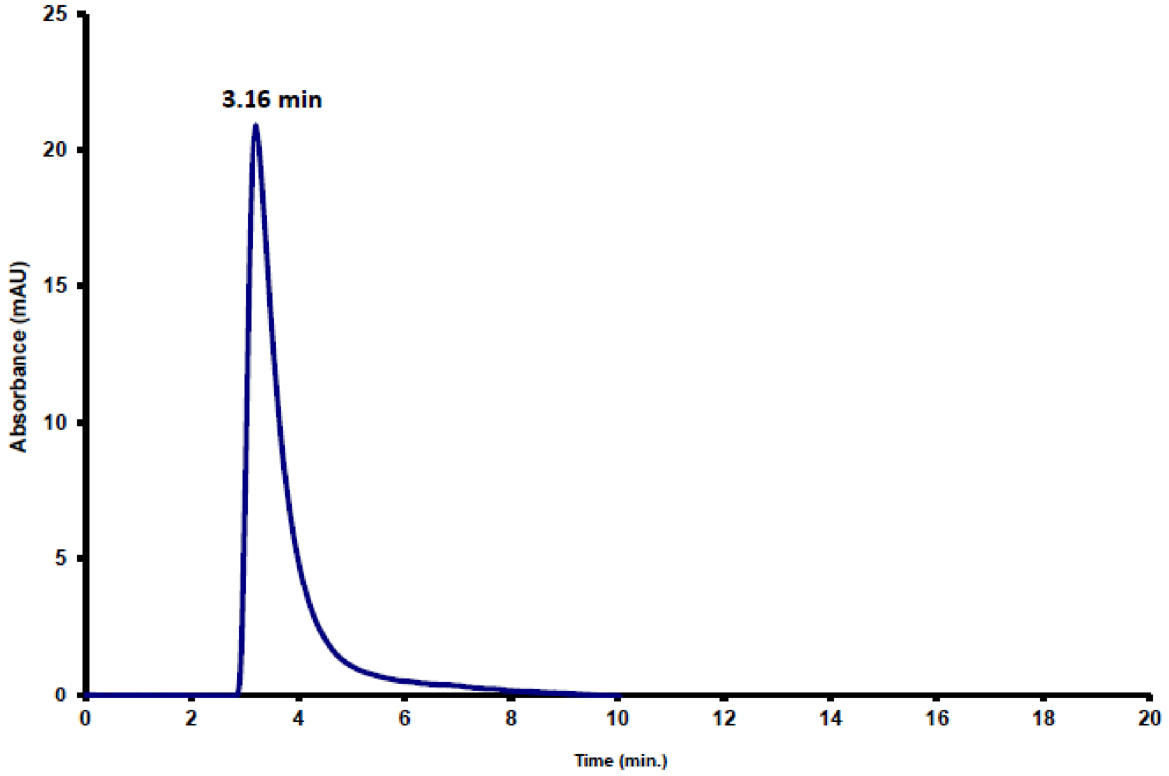


Fig. S5 HPLC chromatogram of **1**

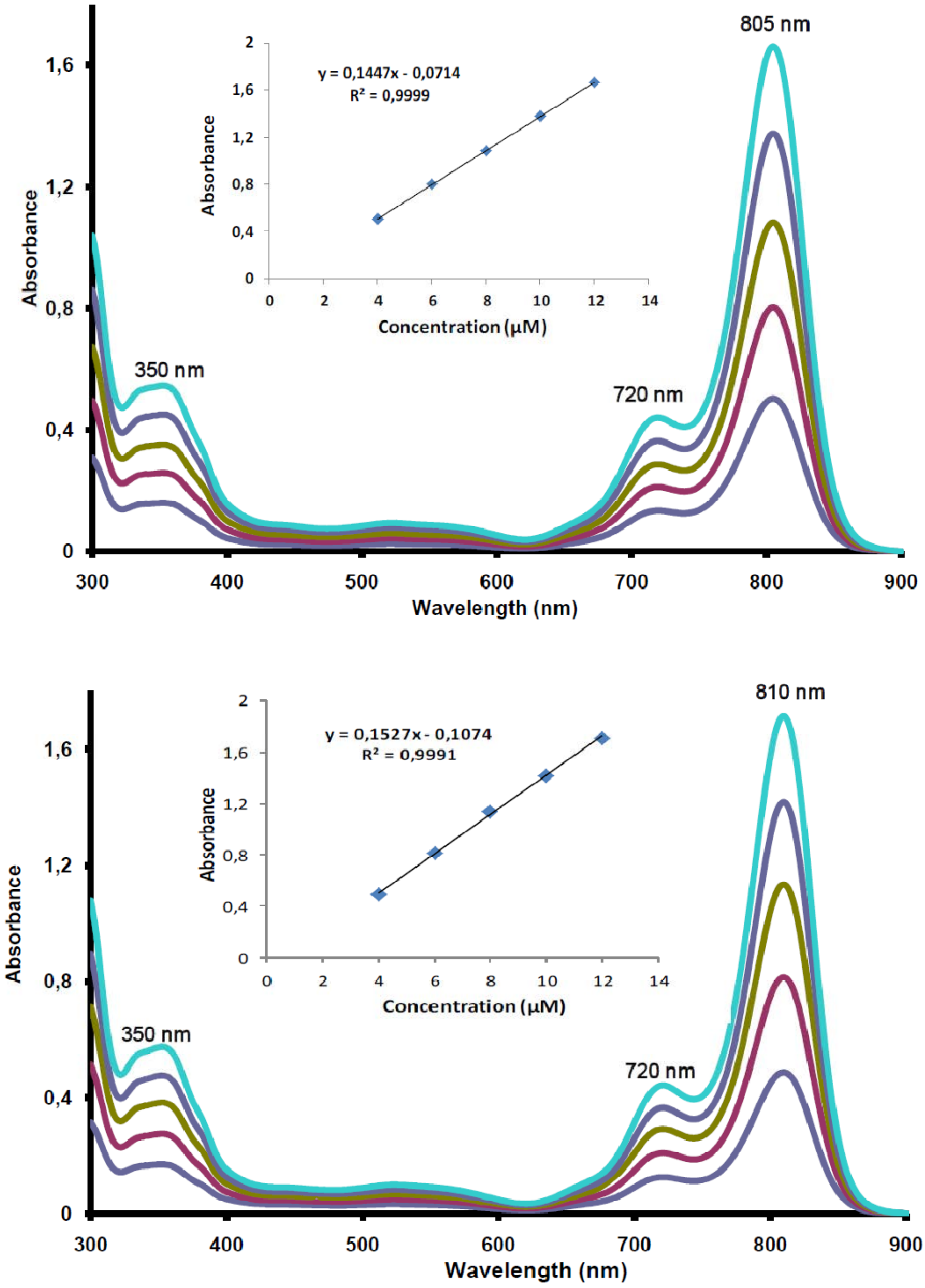


Fig. S6 UV-Vis spectra of **1** (4 to 12 µM) in THF (top) and chloroform (bottom). Insets: plot of absorbance vs concentration

Preparation of phthalocyanine 2

Reaction was initiated from phthalonitrile **4** (300 mg, 0.98 mmol) and yielded 49 mg of a green solid (16 %). $C_{64}H_{82}N_8S_8$, MW 1219.90. m.p. > 300°C. MS (MALDI-TOF) *m/z* 1122.49 [M2H+]. ATR-IR (ν, cm^{-1}) 3307, 2956, 2939, 2920, 2893, 2860, 1551, 1482, 1470, 1452, 1391, 1361, 1279, 1227, 1159, 1141, 1089, 1037, 903, 874, 791, 772, 733, 708. HRMS *m/z* (experimental) 1219,4472; $C_{64}H_{82}N_8S_8$ *m/z* (theoretical) 1219,4501. Error: 2.3 ppm. HPLC t_R (min) 2.75. UV-Vis λmax nm (log ε) in THF: 750 (4.83), 350 (4.49), in $CHCl_3$: 755 (4.83), 350 (4.51).

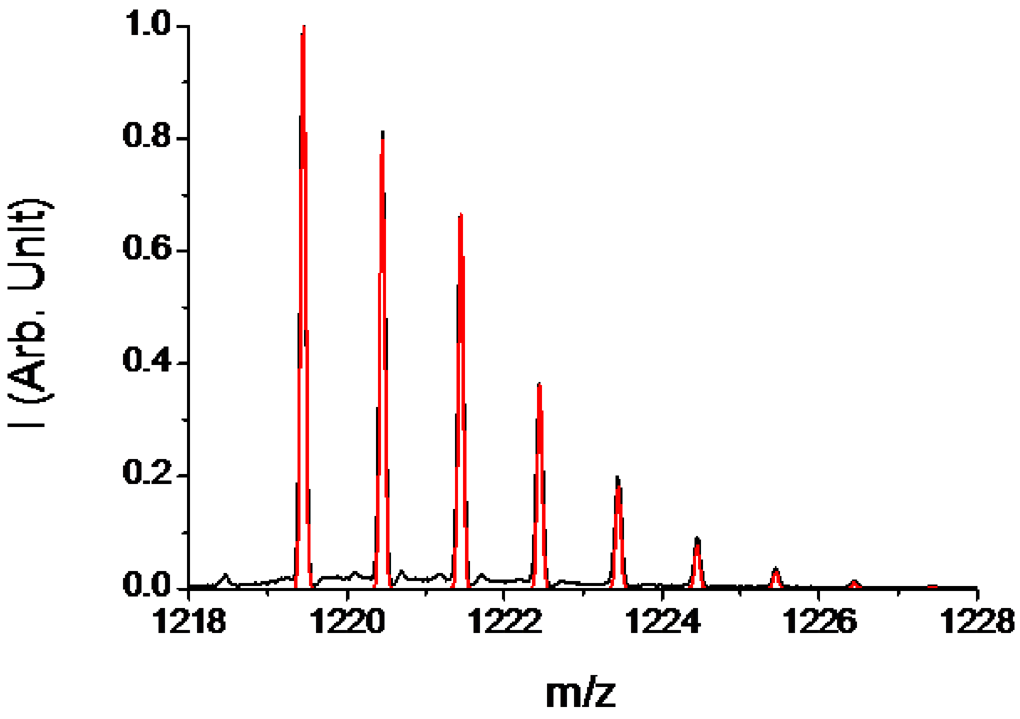


Fig. S7 High resolution mass spectrum (ESI-TOF) of compound **2**. Theoretical (red) and experimental (black) isotopic patterns. m/z (experimental) = 1219,4472; $C_{64}H_{82}N_8S_8$ m/z (theoretical) = 1219,4501. Error: 2.3 ppm. The observed molecular ions in ESI are M^+.

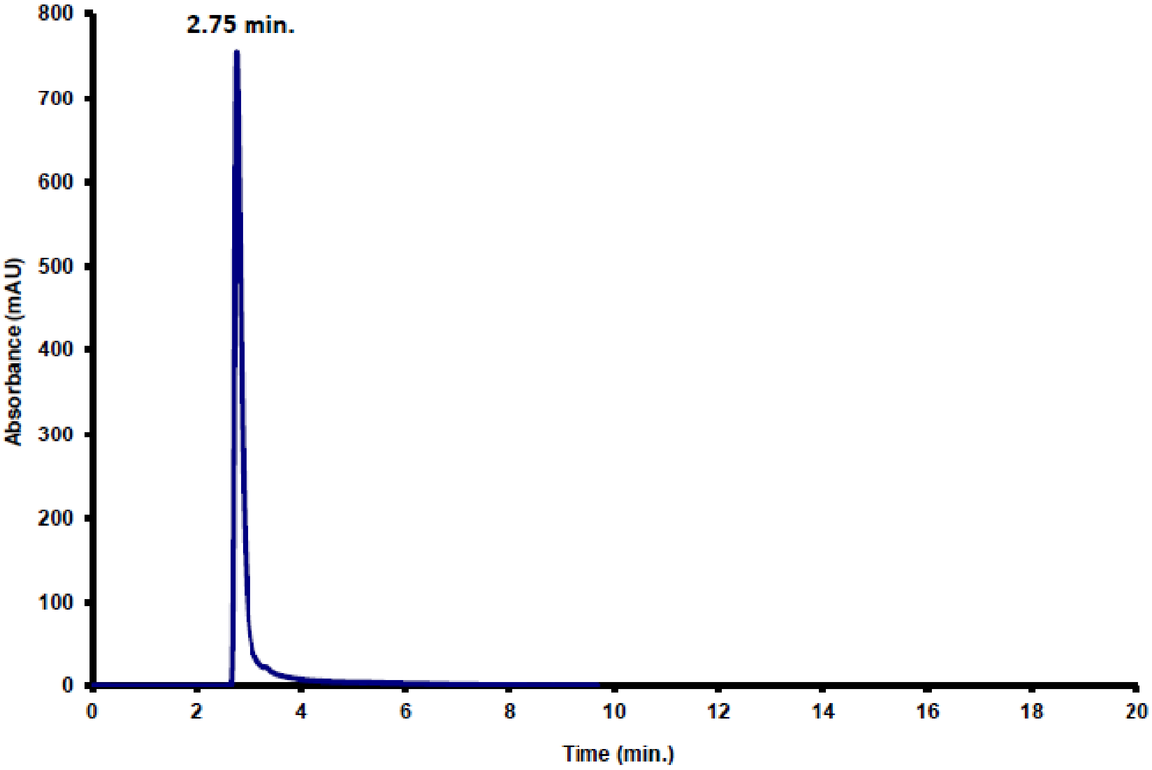
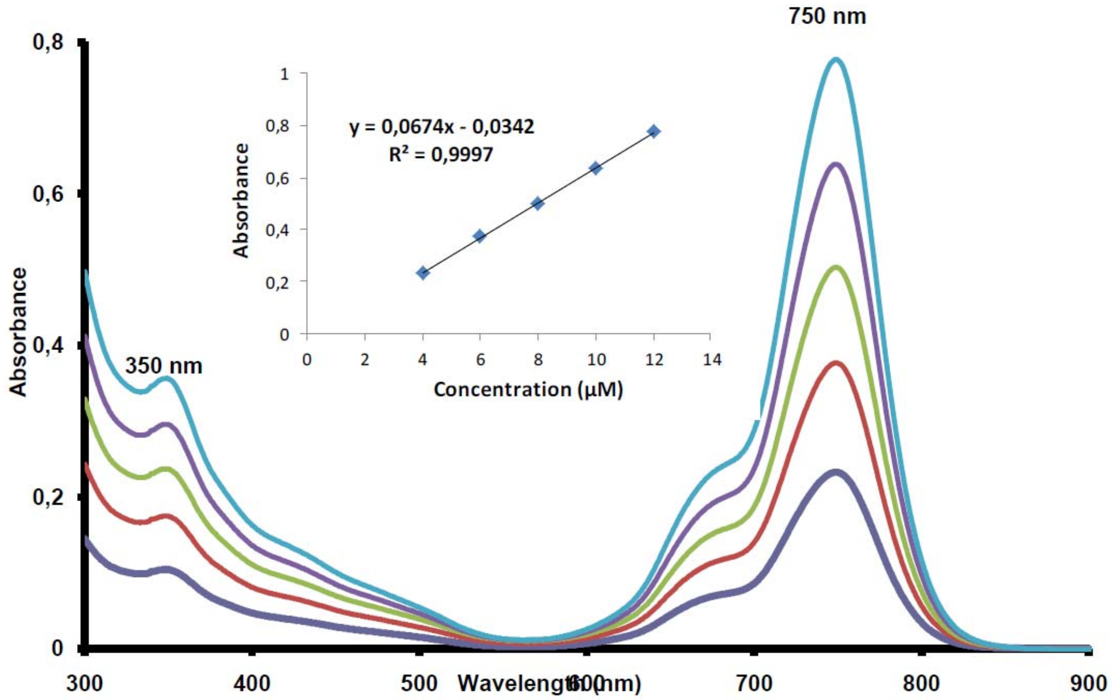


Fig. S8 HPLC chromatogram of **2**



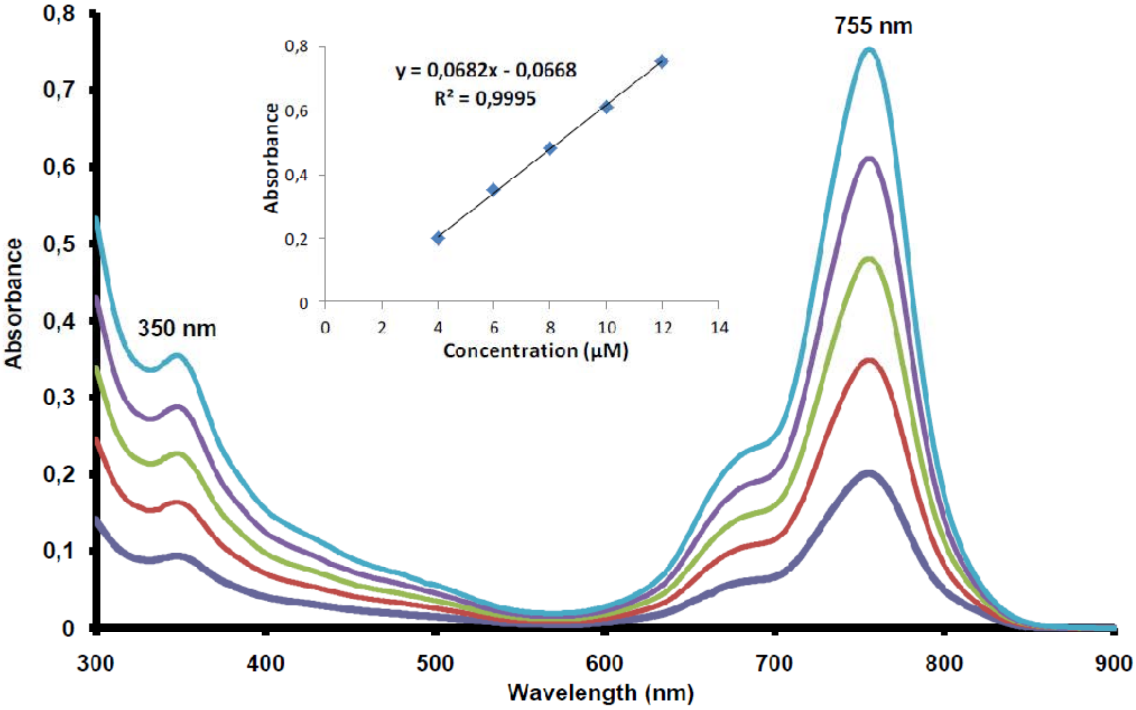
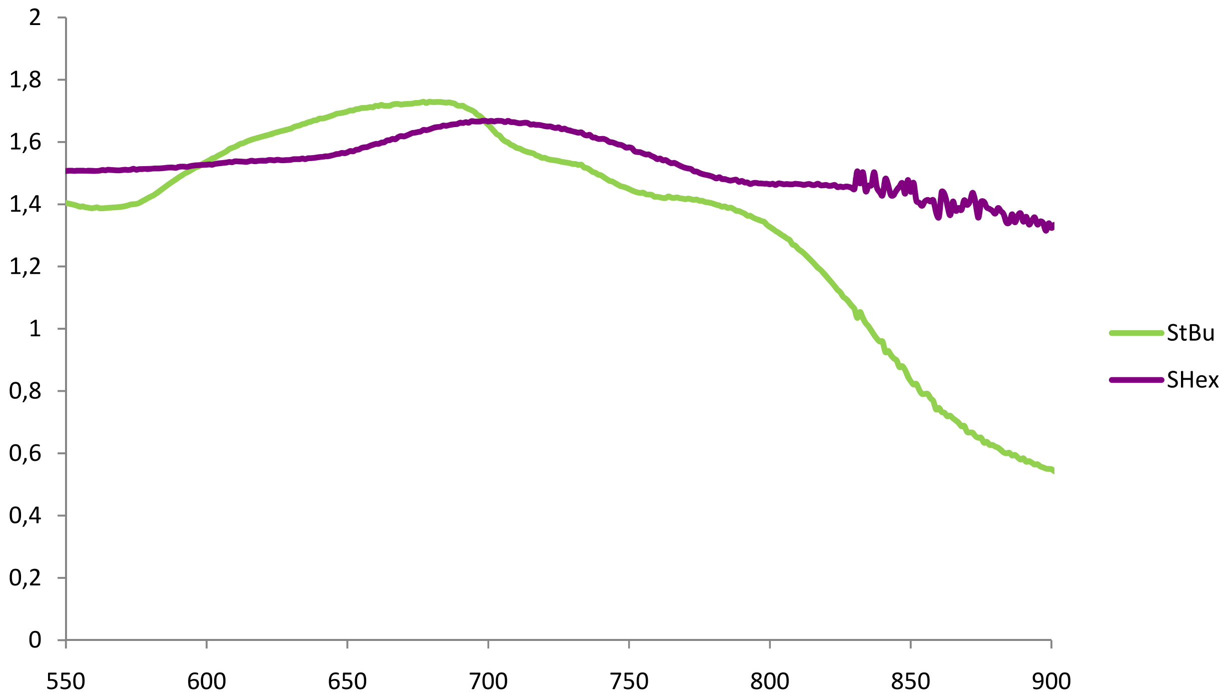


Fig. S9 UV-Vis spectra of **2** (4 to 12 µM) in THF (top) and chloroform (bottom). Insets: plot of absorbance vs concentration



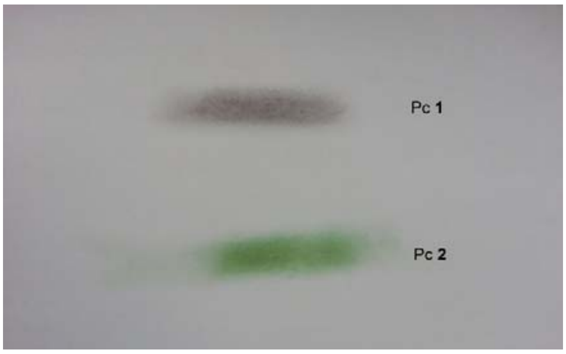


Fig. S10 Top: UV-vis spectrum of phthalocyanines **1** and **2** in solid state (KBr pellets), recorded on UV-2600 Shimadzu spectrophotometer with integration sphere attachment. Bottom: picture of the powder of phthalocyanine **1** and **2** spread out on a white sheet of paper.

X-ray data collection and structure refinement

Unit cell measurements and intensity data collection were performed on an Bruker APEX II QUAZAR three-circle diffractometer using monochromatized Mo *Kα* X-radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS) [5]. Space groups were determined using XPREP implemented in APEX2 [6]. The structure was solved using the direct methods procedure in SIR97 [7], and then refined by full-matrix least-squares refinements on F^2 using the CRYSTALS software [8]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93-0.98 Å) and U_{iso}(H) (in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

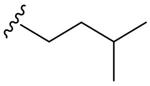
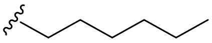
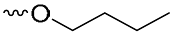
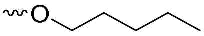
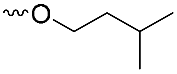
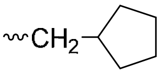
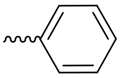
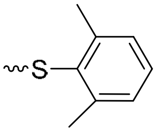
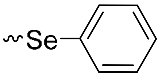
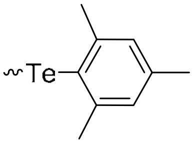
For **1** and **2** metal-free phthalocyanine compounds, internal H atoms attached to the pyrrole nitrogen atoms each have a partial occupancy of 0.5. For compound **2**, the unit cell consists of a large region of disordered solvent which could not be modelled as discrete atomic sites. Herein, the contributions of the disordered solvent molecules were eliminated from the structure using the SQUEEZE algorithm in the PLATON [9] program suite. The final geometrical calculations and the molecular drawings were carried out with PLATON [9] and MERCURY [10] program.

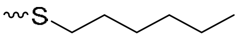
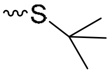
Table S1 Crystal data and refinement parameters for **1** and **2**.

Crystal parameters	**1**	**2**
CCDC	894420	894419
Empirical Formula	$C_{80}H_{114}N_8S_8$	$C_{64}H_{82}N_8S_8$
Formula weight (g.mol^{-1})	1444.37	1219.94
Temperature (K)	120	120
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Cubic
Space group	P-1	P -4 3 n
***a* (Å)**	12.7956 (11)	22.6217 (4)
***b* (Å)**	17.1258 (15)	22.6217 (4)
***c* (Å)**	18.8008 (16)	22.6217 (4)
α(°)	112.281 (4)	90
β(°)	91.994 (5)	90
γ(°)	94.129 (4)	90
Crystal size (mm)	0.50 × 0.16 × 0.11	0.50 × 0.40 × 0.38
V (Å^3)	3793.8 (6)	11576.5 (4)
Z	2	6
ρ_{calcd} (mg.m^{-3})	1.264	1.050
μ (mm^{-1})	0.28	0.27
***F*(000)**	1556	3900
θ range for data collection (°)	1.29 - 25.03	1.27 - 27.52
h*/*k*/*l	-15/14, -20/19, -22/22	-16/16, 0/20, 1/29
Reflections collected	58037	196857
Independent reflections	13404	4450
T_{max} and T_{min}	0.9686 and 0.9554	0.903 and 0.898

Data/restraints/parameters	13404/0/865	4450/19/182
Goodness-of-fit on F^2	0.97	1.01
Final R indices [$I > 2\sigma(I)$]	R_1=0.037, wR_2 = 0.102	R_1=0.063, wR_2 = 0.192
Largest diff. peak and hole (e.Å^{-3})	-0.51 and 0.80	-0.43 and 0.63

Table S2 Crystal Data of all reported structures of unmetallated 1,4,8,11,15,18,22,25-octasubstituted phthalocyanines (R_8PcH_2). Data of entries 1-8 were obtained by a search in Cambridge Structural Database (CSD V. 5.35, Conquest 1.16)

Entry	**Compound (R)**	**CSD Entry Code or CCDC number**	**Crystal System**	**Space Group**	**Deviations from the 4N mean plane**	**λ_{max} (solvent)**	**Ref**
1		WOKDAB	Monoclinic	*C*2/c	Saddle[a] 18° 11.3°	Q_x = 731 nm Q_y = 701 nm THF	[11]
2		SOZBUE	Triclinic	*P*-1	Planar	Data not available	[12]
3		TUXXAL, TUXXAL01	Triclinic	*P*-1	Saddle[b] 14.58° 16.78° 18.27° 18.83°	751 nm 772 nm $CHCl_3$	[13, 14]
4		ILEJAK	Triclinic	*P*-1	Planar	769 nm CH_2Cl_2	[15]
5		SUKSUM	Triclinic	*P*-1	Planar	Data not available	[16]
6		DOTJAY	Tetragonal	*I*41/a	Saddle*[b] 20.36°	Data not available	[17]
7		NUGSEO	Triclinic	*P*-1	Planar	735 nm THF	[18]
8		ECOSOE	Triclinic	*P*-1	Saddle*[b] 21.32° 24.33° 25.02° 17.71°	788 nm $CHCl_3$	[19]
9		CCDC-966681	Monoclinic	*C*2/c	Saddle*[b] 16.73° 12.22°	824 nm CH_2Cl_2	[20]
10		CCDC-966682	Monoclinic	*P21/c*	Saddle*[b] 16.20° 29.93° 5.50° 16.81°	811 nm $CHCl_3$	[20]
11		CCDC-966683	Tetragonal	*P42/nmc*	Saddle*[b] 30.91°	844 nm $CHCl_3$	[20]

12		CCDC-894420	Triclinic	*P*-1	Planar*	810 nm CHCl$_3$	this work
13		CCDC-894419	Cubic	*P*-43n	Saddle*[b] 24.08^{o}	755 nm CHCl$_3$	this work

* Data calculated from the related available cif files.

[a] based on five-membered rings.

[b] based on isoindole rings.

Calculation parameters

The two octa non peripherally alkylsulfonyl substituted Pcs **1** and **2** represented Figure 1 in the paper were computationally modelled using Density Functional Theory (DFT).[21] Various conformations of the substituents were considered. Calculations were performed with Gaussian 09 suite of programs (Revision A.02).[22] Geometries were optimized at spin unrestricted (U) B3LYP hybrid functional[23] using the CEP-31G core potentials[24] and verified to be minima with vibrational frequency calculations. In order to perform a more refined analysis, by using a large number of basis functions, of the electronic structure of **1** and **2**, the non-peripheral substituents were chopped and the resulting structures were capped with methyl groups. Subsequent optimizations of the newly added methyl groups resulted in smaller models of **1** and **2** that could be treated at a higher level of theory (2188 basis functions). Single point energy calculations on these structures were performed with B3LYP hybrid functional employing the Dunning type cc-pVTZ basis set[25] from which Kohn-Sham orbital energies discussed in the main text were obtained.

Initial trials from various conformers were performed with semi-empirical AM1[26] and PM3[27] methods as well as B3LYP and Coulomb attenuated CAM-B3LYP[28] density functionals using various basis sets. No restrictions on symmetry were imposed.

Table S3 DFT Results at CAM-B3LYP/CEP-31G Level of Theory

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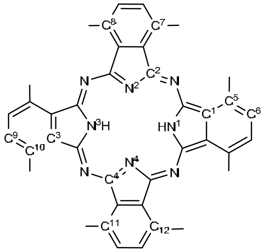
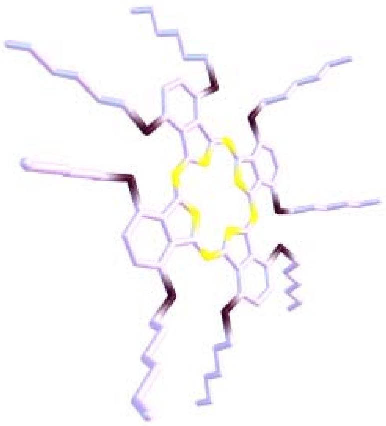
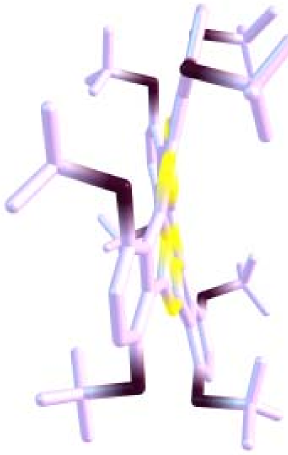
<tr><td colspan="2"> </td></tr>
<tr><td></td><td></td></tr>
<tr><td>1</td><td>2</td></tr>
<tr><td>LESS DISTORTED
$\angle C^8N^2N^4C^{12} = 33°$</td><td>MORE DISTORTED
$\angle C^8N^2N^4C^{12} = 87°$</td></tr>
<tr><td>LESS PERTURBED π-SYSTEM</td><td>MORE PERTURBED π-SYSTEM</td></tr>
<tr><td colspan="2">~60 nm red shift in absorption of 1 compared to 2</td></tr>
<tr><td colspan="2">CAM-B3LYP in G09 is used, hydrogens are excluded for clarity.</td></tr>
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Table S4. MO Energies and Electrostatic Potential Charges[a] at UB3LYP/cc-pVTZ + Solvation (SCRF, Solvent=THF) Level of Theory

Species	**MO**	**E(eV)**	**ΔE(LUMO - HOMO)**		**Charge**[a]
			(eV)	(nm)	
1	LUMO	-3.11			-0.24
	HOMO	-4.77	1.66	748	
2	LUMO	-3.08			-0.21
	HOMO	-4.86	1.78	698	

[a] Average charge computed for S atoms.

Cartesian Coordinates

1’

UB3LYP/cc-pVTZ, 2S+1=1

E_{tot} = -5169.242802 A.U.

	x(Å)	y(Å)	z(Å)
C	4.574397	-3.387222	9.188567
H	5.455035	-3.539332	8.559661
H	4.057411	-4.337425	9.345233
C	9.792910	-7.594437	11.825198
H	10.653982	-8.194335	12.129585
H	9.937281	-7.277193	10.789390
C	12.552476	2.639278	21.664490
H	13.003262	3.551899	21.265590
H	11.792400	2.889464	22.408546
C	13.047653	-7.117832	15.731012
H	14.072828	-6.757461	15.614606
H	12.906703	-7.539524	16.729357
C	14.541688	-1.982677	20.596519
H	15.411483	-2.123328	19.949532
H	14.292709	-2.918835	21.101999
C	1.419904	-0.075390	11.644370
H	1.173645	-0.833009	10.896975
H	0.705395	-0.153408	12.467638
C	7.236486	6.612129	18.851716
H	8.194795	7.067837	18.589160
H	6.434616	7.238616	18.453768
C	2.792868	5.076365	16.528676
H	2.625217	5.554921	15.560429
H	1.913744	4.497128	16.820764
H	13.335641	2.050655	22.148338
H	7.129874	6.559121	19.938199
H	2.962705	5.853573	17.277621
H	1.353143	0.911228	11.178843
H	3.892903	-2.700748	8.680578
H	8.894752	-8.211359	11.909762
H	12.869869	-7.903252	14.992771
H	14.789797	-1.232568	21.351322
S	4.315243	4.072005	16.547548
C	3.968626	2.822116	15.356121
C	4.903459	1.797660	15.093847
C	4.643018	0.794077	14.118348
C	5.787004	-0.106774	14.109496
N	5.951023	-1.131710	13.281711
C	6.956996	-2.016022	13.364506
N	7.960818	-2.033253	14.287238
C	8.659360	-3.192792	14.120431
N	9.701546	-3.625926	14.844244
C	10.248620	-2.975949	15.863137
N	9.922471	-1.720464	16.330231
C	10.727630	-1.329329	17.373424
N	10.646826	-0.214594	18.089600
C	9.731013	0.748843	17.897798
N	8.680514	0.721466	17.026793
C	7.987962	1.888952	17.177110
N	6.831275	2.228167	16.591290
C	6.210382	1.516698	15.664219
N	6.663274	0.365507	15.056528
H	7.533194	-0.089257	15.311164
C	8.638404	2.752341	18.179339
C	9.747361	2.013522	18.646086
C	10.573143	2.511320	19.678518
S	11.896806	1.554127	20.352341
C	10.289502	3.802472	20.150645
C	9.220849	4.542321	19.658730
C	8.355241	4.039436	18.675767
S	7.002540	4.990333	18.047942
H	9.093034	5.556318	20.009875
H	10.963267	4.292975	20.832626
C	11.663574	-2.420051	17.621812
C	11.373936	-3.433703	16.664712
C	12.138733	-4.617824	16.587992
S	11.813179	-5.829792	15.348657
C	13.160002	-4.751745	17.536760
C	13.453321	-3.757125	18.470947
C	12.729544	-2.563422	18.537948
S	13.113827	-1.288996	19.696396
H	14.351363	-3.906546	19.044790
H	13.787510	-5.633743	17.543356
H	9.089616	-1.195730	16.092258
C	8.104347	-3.970558	12.992532
C	7.028140	-3.198914	12.507040
C	6.270479	-3.598134	11.394242
S	5.001036	-2.554046	10.756002
C	6.574633	-4.850364	10.835500
C	7.624162	-5.621944	11.321861
C	8.428798	-5.203133	12.399075
S	9.779443	-6.181661	12.979514
H	7.780629	-6.602643	10.895384
H	5.915766	-5.293197	10.110819
C	3.434552	0.771269	13.384641
S	3.120117	-0.476121	12.169607
C	2.512397	1.776555	13.688226
C	2.776504	2.772228	14.629357
H	2.007976	3.518131	14.786964
H	1.523107	1.784125	13.256021

2’

UB3LYP/cc-pVTZ, 2S+1=1

E_{tot} = -5169.2570696 A.U.

	x(Å)	y(Å)	z(Å)
C	-29.947128	-13.117077	-7.777527
H	-29.688258	-13.410063	-8.798098
H	-30.387218	-13.963677	-7.244088
H	-30.684799	-12.312365	-7.819751
C	-24.870085	-18.405997	-8.049793
H	-25.714260	-18.849024	-7.514686
H	-25.190806	-18.062165	-9.036281
H	-24.099903	-19.170124	-8.176856
C	-20.814159	-18.651986	-3.540986
H	-19.977247	-19.099776	-4.082900
H	-20.509890	-18.394493	-2.523474
H	-21.626197	-19.381138	-3.490703
C	-15.521358	-13.571857	-3.258859
H	-15.866817	-13.883936	-2.270156
H	-15.083582	-14.420952	-3.790157
H	-14.754407	-12.803875	-3.137160
C	-15.302009	-9.507202	-7.772544
H	-14.558462	-10.307042	-7.800075
H	-15.555281	-9.227145	-8.798174
H	-14.874313	-8.651679	-7.243727
C	-20.390649	-4.214266	-8.042011
H	-20.075519	-4.549477	-9.033261
H	-21.163068	-3.450534	-8.158070
H	-19.544481	-3.775639	-7.507039
C	-24.448590	-3.980637	-3.543039
H	-24.745097	-4.237745	-2.523026
H	-23.646076	-3.240978	-3.499784
H	-25.294022	-3.546327	-4.082877
C	-29.739192	-9.061755	-3.264333
H	-30.510041	-9.829050	-3.161936
H	-29.406054	-8.763237	-2.267351
H	-30.169094	-8.205318	-3.790167
S	-16.730637	-10.219267	-6.889891
C	-17.916125	-8.896797	-6.965448
C	-19.218772	-9.089302	-6.475009
C	-20.195592	-8.070874	-6.533373
C	-19.922507	-6.805838	-7.081497
S	-21.185919	-5.555557	-7.095070
C	-18.610061	-6.612532	-7.544337
C	-17.641811	-7.619098	-7.480996
H	-16.645635	-7.378992	-7.831633
H	-18.304103	-5.642735	-7.915333
C	-21.414895	-8.672772	-5.977332
N	-21.224757	-9.994059	-5.711979
C	-19.906308	-10.259080	-5.916027
N	-19.275014	-11.398475	-5.607467
S	-21.520681	-17.218920	-4.420959
C	-20.198421	-16.035572	-4.345402
C	-20.398155	-14.728210	-4.835841
C	-19.370385	-13.745660	-4.777477
C	-18.101479	-14.028198	-4.229353
S	-16.850218	-12.768744	-4.215780
C	-17.914994	-15.336513	-3.766513
C	-18.925219	-16.305809	-3.829854
H	-18.684935	-17.301642	-3.479217
H	-16.946338	-15.645374	-3.395517
C	-19.918768	-12.518564	-5.333518
N	-21.241297	-12.775549	-5.598871
C	-21.578313	-14.090080	-5.394823
N	-22.729972	-14.658454	-5.703383
H	-21.906589	-12.058521	-5.856758
S	-28.519601	-12.406705	-6.889891
C	-27.334419	-13.729569	-6.965448
C	-26.031417	-13.537569	-6.475009
C	-25.054721	-14.556217	-6.533373
C	-25.328934	-15.821006	-7.081497
S	-24.067974	-17.073231	-7.095070
C	-26.641317	-16.013829	-7.544337
C	-27.609262	-15.007046	-7.480996
H	-28.605530	-15.246730	-7.831633
H	-26.947362	-16.983679	-7.915333
C	-23.835266	-13.954720	-5.977332
N	-24.025375	-12.633537	-5.711979
C	-25.343681	-12.368046	-5.916027
N	-25.974978	-11.228613	-5.607467
S	-23.728627	-5.408399	-4.420959
C	-25.050533	-6.591822	-4.345402
C	-24.851597	-7.899008	-4.835841
C	-25.879696	-8.881197	-4.777477
C	-27.148888	-8.597730	-4.229353
S	-28.400959	-9.856920	-4.215780
C	-27.334235	-7.289461	-3.766513
C	-26.323522	-6.320752	-3.829854
H	-26.563621	-5.324835	-3.479217
H	-28.302664	-6.980211	-3.395517
C	-25.331437	-10.108427	-5.333518
N	-24.008887	-9.851657	-5.598871
C	-23.671761	-8.537251	-5.394823
N	-22.520069	-7.968975	-5.703383
H	-23.343654	-10.568724	-5.856758

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checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: 1

```
Bond precision:  C-C = 0.0027 A          Wavelength=0.71073

Cell:          a=12.7956(11)      b=17.1258(15)    c=18.8008(16)
               alpha=112.281(4)   beta=91.994(5)   gamma=94.129(4)
Temperature:   120 K

                Calculated                 Reported
Volume          3793.8(6)                  3793.8(6)
Space group     P -1                       P -1
Hall group      -P 1                       -P 1
Moiety formula  C80 H114 N8 S8             C80 H114 N8 S8
Sum formula     C80 H114 N8 S8             C80 H114 N8 S8
Mr              1444.28                    1444.37
Dx,g cm-3       1.264                      1.264
Z               2                          2
Mu (mm-1)       0.285                      0.285
F000            1556.0                     1556.0
F000’           1558.39
h,k,lmax        15,20,22                   15,20,22
Nref            13430                      13404
Tmin,Tmax       0.947,0.969                0.955,0.969
Tmin’           0.868

Correction method= # Reported T Limits: Tmin=0.955 Tmax=0.969
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.028

R(reflections)= 0.0372( 11476)    wR2(reflections)= 0.1021( 13404)

S = 0.970                  Npar= 865
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        3.9 Ratio
PLAT222_ALERT_3_C Large Non-Solvent  H     Uiso(max)/Uiso(min) ...        4.4 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C58    --  C59     ..        6.1 su
```

Alert level G

```
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          4 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT808_ALERT_5_G No Parseable SHELXL Style Weighting Scheme Found     Please Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   3 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

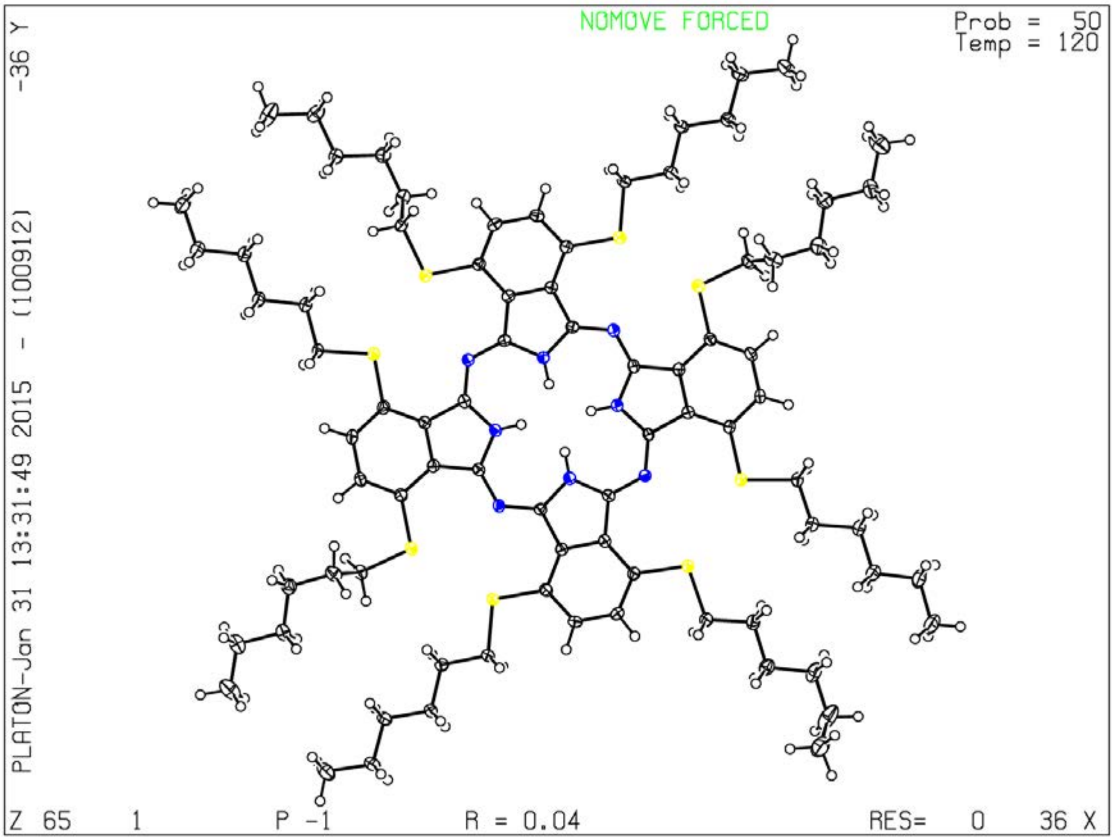
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 29/01/2015; check.def file version of 29/01/2015

Datablock 1 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: 1

```
Bond precision:  C-C = 0.0071 A          Wavelength=0.71073

Cell:            a=22.6217(4)     b=22.6217(4)     c=22.6217(4)
                 alpha=90         beta=90          gamma=90
Temperature:     120 K

                Calculated                  Reported
Volume          11576.5(6)                  11576.5(4)
Space group     P -4 3 n                    P -4 3 n
Hall group      P -4n 2 3                   P -4n 2 3
Moiety formula  C64 H82 N8 S8               C64 H82 N8 S8
Sum formula     C64 H82 N8 S8               C64 H82 N8 S8
Mr              1219.86                     1219.94
Dx,g cm-3       1.050                       1.050
Z               6                           6
Mu (mm-1)       0.270                       0.268
F000            3900.0                      3900.0
F000’           3906.95
h,k,lmax        29,29,29                    16,20,29
Nref            4446[ 2397]                 4450
Tmin,Tmax       0.879,0.903                 0.898,0.903
Tmin’           0.875

Correction method= # Reported T Limits: Tmin=0.898 Tmax=0.903
AbsCorr = MULTI-SCAN

Data completeness= 1.86/1.00      Theta(max)= 27.517

R(reflections)= 0.0625( 3464)     wR2(reflections)= 0.1917( 4450)

S = 1.009                 Npar= 182
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT230_ALERT_2_C Hirshfeld Test Diff for    S6     --  C5      ..        6.0 su
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....         S6 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0071 Ang.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
              C64 H82 N8 S8
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          5 Report
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............           1 Report
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...          2 Units
PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of .        313 A**3
PLAT808_ALERT_5_G No Parseable SHELXL Style Weighting Scheme Found     Please Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         19 Note
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed           ! Info
PLAT950_ALERT_5_G Calculated (ThMax) and CIF-Reported Hmax Differ          13 Units
PLAT951_ALERT_5_G Calculated (ThMax) and CIF-Reported Kmax Differ           9 Units
```

```
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   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

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   5 ALERT type 5 Informative message, check
```

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A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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PLATON version of 29/01/2015; check.def file version of 29/01/2015

Datablock 1 - ellipsoid plot