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Supporting Information

69451 Weinheim, Germany

Phosphorescent, Terdentate, Liquid-crystalline Complexes of Platinum(II): Stimulus-dependent Emission

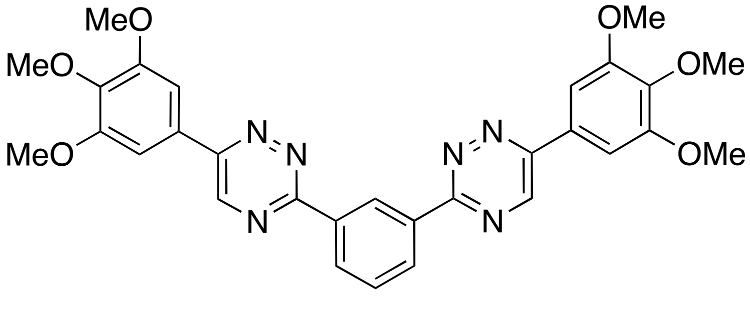
Valery N. Kozhevnikov, Bertrand Donnio and Duncan W. Bruce

Supplementary Information

Materials and Methods. Solvents were purified by using standard methods and dried when necessary. All commercially available reagents were used as received. TLC was carried out on silica gel Si 60-F254. Column chromatography was carried out on silica gel Si 60, mesh size 0.040-0.063 mm (Merck, Darmstadt, Germany). Nuclear magnetic resonance spectra were recorded on a Jeol JNM-EX 270 FT NMR system at 270 MHz for ^{1}H NMR and 68 MHz for ^{13}C NMR. UV-Vis and Infrared spectra were obtained by using a Shimadzu UV-2401 PC and Shimadzu IR Prestige-21 spectrometers, respectively. UV-Vis spectra were obtained using a Shimadzu UV-2401 PC instrument. on Microanalyses were performed at the Department of Chemistry, University of York. using Exeter Analytical Inc. CE 440 instrument. Hitachi F-4500 fluorescence spectrophotometer was used for recording emission and excitation spectra. All solutions for luminescence measurements were degassed by bubbling argon through the solutions for 20 min. A solution of *tris*(bipyridine)ruthenium(II) chloride $[Ru(bipy)_3]Cl_2$ in water ($\phi = 0.042$) was used as a reference in determination of quantum yields in solution. The phase transition temperatures were determined using Mettler Toledo DSC-822e differential scanning calorimeter with a heating and cooling rate of 10 °C min^{-1} (the apparatus was calibrated with indium, 156.6 °C). Texture observations were made using Olympus BX50 polarizing microscope in conjunction with a Linkam LTS350 hot stage and Linkam TMS92 control unit. Literature procedures were followed for the preparation of starting 1,3-[5-(3,4,5-trimethoxyphenyl)-1,2,4-triazine-4-oxide-2-yl]-benzene [1].

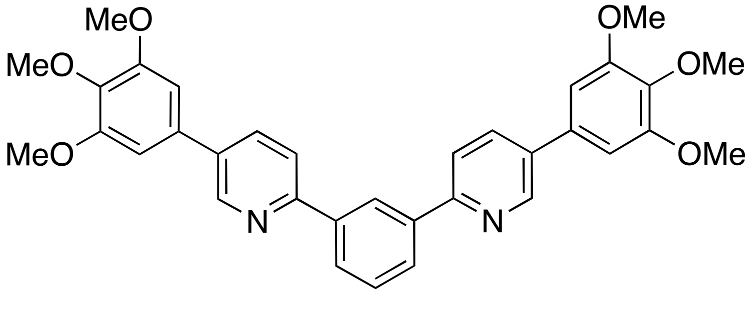
The XRD patterns were obtained with two different experimental set-ups. In all cases, a linear, monochromatic Cu-Kα_1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like geometry was used in the second experimental set-up. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall thickness. An initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature controlled to within ± 0.3 °C from 20 to 350 °C. The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature controlled to within ± 0.05 °C from 20 to 200 °C. Exposure times were varied from 2 to 8 h.

1,3-[5-(3,4,5-trimethoxyphenyl)-1,2,4-triazine-2-yl]-benzene, 2



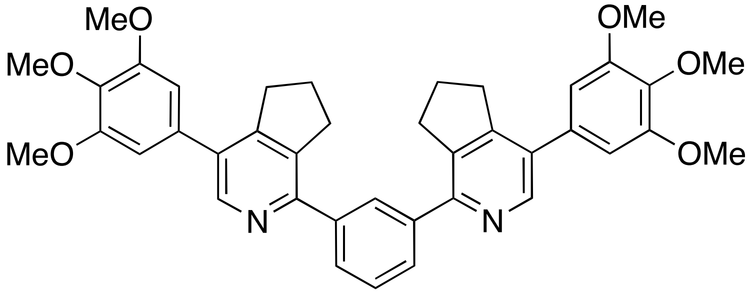
A suspension of 1,3-[5-(3,4,5-trimethoxyphenyl)-1,2,4-triazine-4-oxide-2-yl]-benzene (15 g, 25 mmol) in triethylphosphite (50 cm^3) was heated under reflux for 12 h. The reaction mixture was allowed to cool room temperature; solid was filtered off and washed with ethanol to give required compound. Yield 13.9 g, 98%; δ_H ($CDCl_3$): 3.95 (s, 3H), 4.00 (s, 6H), 7.43 (s, 2H), 7.75 (t, $^3J_{HH}$ 7.7 Hz, 1H), 8.79 (dd, $^3J_{HH}$ 7.7 Hz, $^4J_{HH}$ 1.8 Hz, 2H), 9.07 (s, 2H), 9.76 (t, $^4J_{HH}$ 1.8 Hz, 1H)

1,3-[5-(3,4,5-trimethoxyphenyl)pyridine-2-yl]-benzene, 3-1



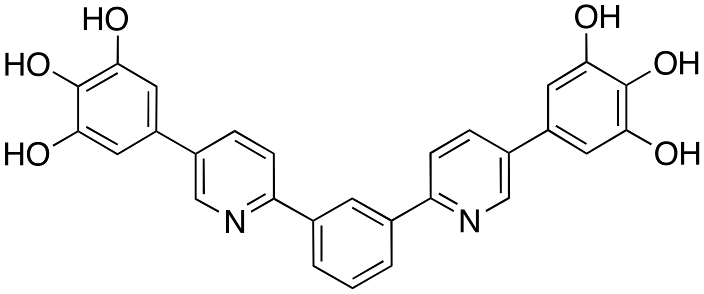
An autoclave equipped with a stirring bar was charged with the 1,3-[5-(3,4,5-trimethoxyphenyl)-1,2,4-triazine-2-yl]-benzene (3 g, 5.3 mmol), xylene (50 cm^3) and norbornadiene (5.4 cm^3, 53 mmol). The autoclave was sealed, placed in oil bath and heated at 200 °C (bath) for 24 h. The reaction mixture was filtered through a small pad of silica gel while hot; the silica gel was washed with DCM until no product was present in the filtrate (as checked by TLC). All filtrates were combined and the solvent was removed under reduced pressure. The residue was triturated with ethanol, the formed solid was filtered off and washed with ethanol to give the desired product. Yield 2.6 g, 87%; δ_H ($CDCl_3$): 3.91 (s, 3H), 3.98 (s, 6H), 6.82 (s, 2H), 7.63 (t, $^3J_{HH}$ 7.7 Hz, 1H), 7.94 (br. s, 4H), 8.11 (dd, $^3J_{HH}$ 7.7 Hz, $^4J_{HH}$ 1.8 Hz, 2H), 8.74 (t, $^4J_{HH}$ 1.8 Hz, 1H), 8.93 (br. s, 2H).

1,3-[5-(3,4,5-trimethoxyphenyl)-3,4-cyclopentenopyridine-2-yl]-benzene, 4-1

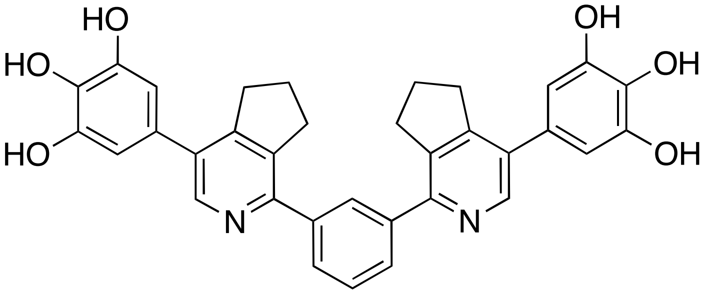


A mixture of 1,3-[5-(3,4,5-trimethoxyphenyl)-1,2,4-triazine-2-yl]benzene (1.7 g, 2.07 mmol) and 1-morpholinocyclopentene (3 cm^3, 18.8 mmol) were stirred at 190 °C under an argon atmosphere for 1 h, after which 1-morpholinocyclopentene (1 cm^3, 6.3 mmol) was added and the reaction mixture was stirred at 190 °C for additional hour. Ethanol (10 cm^3) was added; the solid formed was separated by filtration and washed with cold ethanol (5 cm^3). Yield 1.01 g, 76 %; δ_H ($CDCl_3$): 2.1 (m, 4H), 3.07 (t, J = = 7.3 Hz, 4H), 3.22 (t, J = = 7.3 Hz, 4H), 3.98 (br.s, 18H), 6.68 (s, 2H), 7.59 (t, J = 7.7 Hz, 1H), 7.85 (br.d, J = 7.7 Hz, 2H), 7.94 (br. s, 4H), 8.56 (s, 2H)

1,3-[5-(3,4,5-trihydroxyphenyl)pyridine-2-yl]-benzene



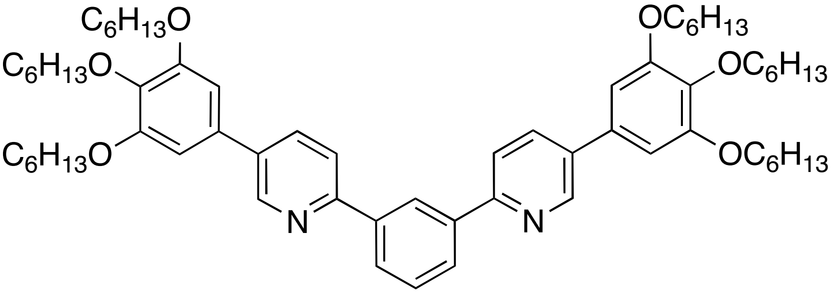
The mixture of anhydrous pyridinium chloride[2] (35.0 g) and 1,3-[5-(3,4,5-trimethoxyphenyl)pyridine-2-yl]benzene (7 g, 12.4 mmol) was stirred at 200 °C for 12 h. The hot solution was quenched carefully with water (50 cm^3). The resulting precipitate was filtered off, washed thoroughly with water, hot acetone, and dried in vacuum to yield the desired product (5.3 g, 89 %). δ_H (DMSO-d_6) = 6.74 (s, 4H), 7.73 (t, J = 7.7 Hz, 1H), 8.21 (br. d, J = 7.7 Hz, 2H), 8.26 (br. s, 4H), 8.81 (br. s, 1H), 8.87 (br. s, 2H).



δ_H (DMSO-d_6) = 2.14 (q, *J* = 7.3, 4H), 3.23 (t, *J* = 7.3, 4H), 3.24 (t, *J* = 7.3, 4H), 6.61 (s, 4H), 7.87 (t, *J* = 7.7 Hz, 1H), 8.06 (br. d, *J* = 7.7 Hz, 2H), 8.23 (br. s, 1H), 8.58 (s, 2H).

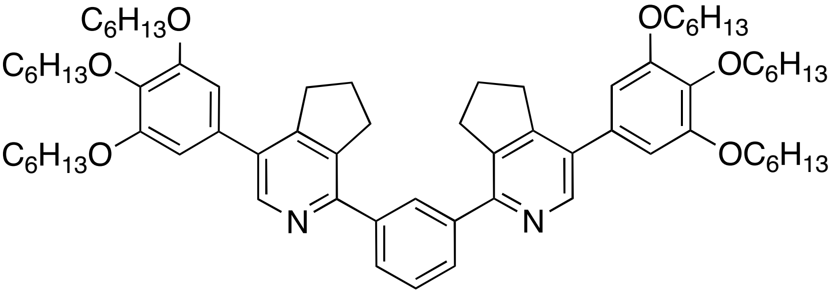
Preparation of ligands 3-*n* and 4-*n*

1,3-[5-(3,4,5-trihexyloxyphenyl)pyridine-2-yl]benzene 3-*6*



A mixture of 1,3-[5-(3,4,5-trihydroxyphenyl)pyridine-2-yl]-benzene (247 mg, 0.51 mmol), potassium carbonate (1056 mg, 7.65 mmol), 1-bromohexane (841 mg, 5.1 mmol) and DMF (10 cm^3) was stirred at 100°C for 12 h. The solvent was removed under reduced pressure; the product was purified by column chromatography (silica gel, DCM/petrol ether/ethyl acetate 10/10/1) to give the titled compound. Yield (426 mg, 85%). δ_H ($CDCl_3$, 270 MHz): 0.89 (m, 18H), 1.34 (m, 24 H), 1.49 (m, 12H), 1.73 - 1.86 (m, 12H), 3.99 (t, *J* = 6.7 Hz, 4H), 4.05 (t, *J* = 6.7 Hz, 8H), 6.79 (s, 4H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.89 (dd, *J* = 8.2 Hz, *J* = 0.9 Hz, 2H), 7.92 (dd, *J* = 8.2 Hz, *J* = 2.1 Hz, 2H), 8.09 (dd, *J* = 7.7 Hz, *J* = 1.8 Hz, 2H), 8.71 (t, *J* = 1.8 Hz, 1H), 8.90 (dd, *J* = 2.1 Hz, *J* = 0.9 Hz, 2H). Other homologues were prepared in the same way.

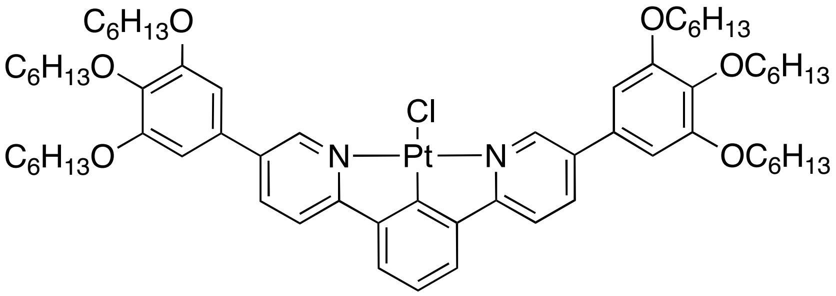
4-6



The compound **4**-*6* was prepared analogously to **3**-*6*. Column chromatography was used for purification using silica gel and 4:1 petrol ether : ethyl acetate mixture as eluent. δ_H ($CDCl_3$, 270 MHz): 0.89 (m, 18H), 1.33 (m, 24 H), 1.49 (m, 12H), 1.73 - 1.86 (m, 12H), 2.07 (4H, q, *J* = 7.3), 3.06 (4H, t, *J* = 7.3), 3.20 (4H, t, *J* = 7.3), 3.95 (t, *J* = 6.7 Hz, 4H), 3.96 (t, *J* = 6.7 Hz, 8H), 6.65 (s, 4H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.81 (dd, *J* = 8.2 Hz, *J* = 0.9 Hz, 2H), 8.14 (t, *J* = 1.8 Hz, 1H), 8.55 (s, 2H). Other homologues were prepared in the same way.

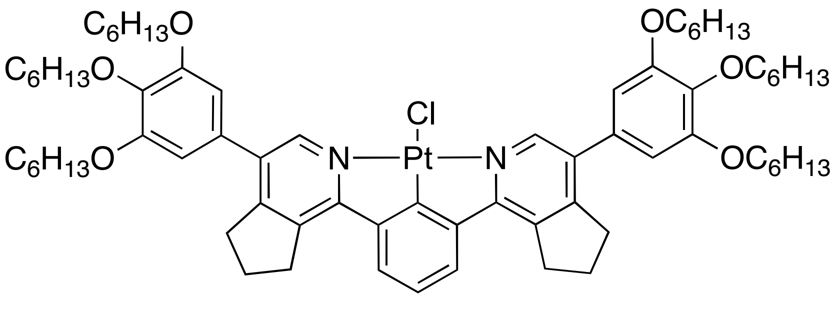
Preparation of platinum(II) complexes **5**-*n* and **6**-*n*.

5-6



A mixture of 1,3-[5-(3,4,5-trihexyloxyphenyl)pyridine-2-yl]benzene **3**-*6* (268 mg, 0.27 mmol), potassium tetrachloroplatinate (113 mg, 027 mmol) and acetic acid (50 cm^3) was heated under reflux under a nitrogen atmosphere for 24 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, DCM, R*f* ≈ 0.8) to give **5**-*6*. Yield 67%, δ_H ($CDCl_3$, 270 MHz): 0.85 (m, 18H), 1.3 (m, 24 H), 1.5 (m, 12H), 1.71 (q, *J* = 6.7 Hz, 4H), 1.76 (q, *J* = 6.7 Hz, 8H), 3.94 (t, *J* = 6.7 Hz, 4H), 3.98 (t, *J* = 6.7 Hz, 8H), 6.70 (s, 4H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.96 (dd, *J* = 8.5 Hz, *J* = 2.2 Hz, 2H), 9.46 (d, 2H, *J* = 2.2 Hz, $^3J_{HPt}$ 37.4 Hz). Other homologues were prepared in the same way.

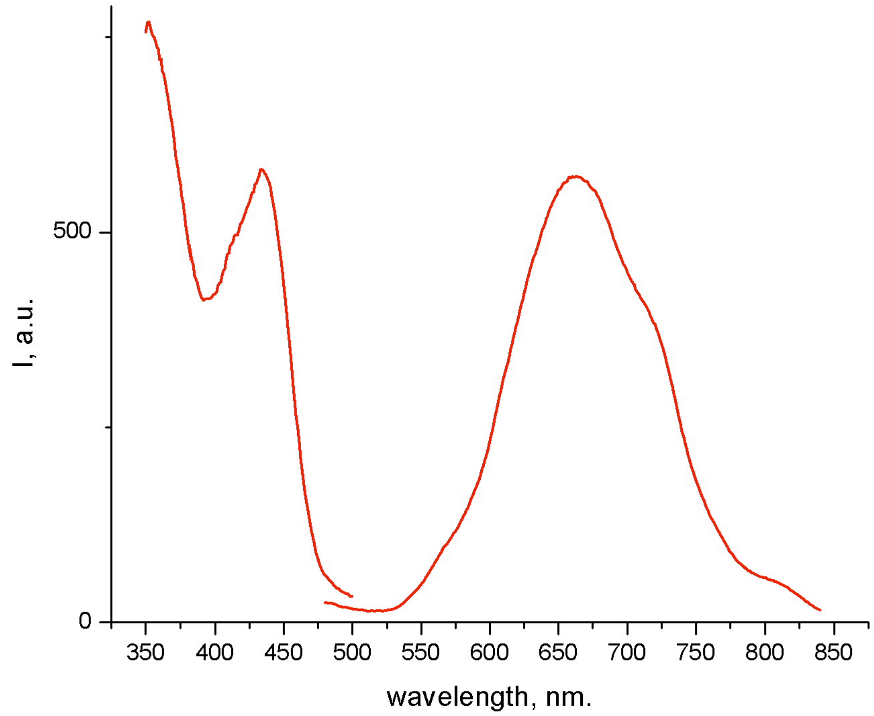
6-6



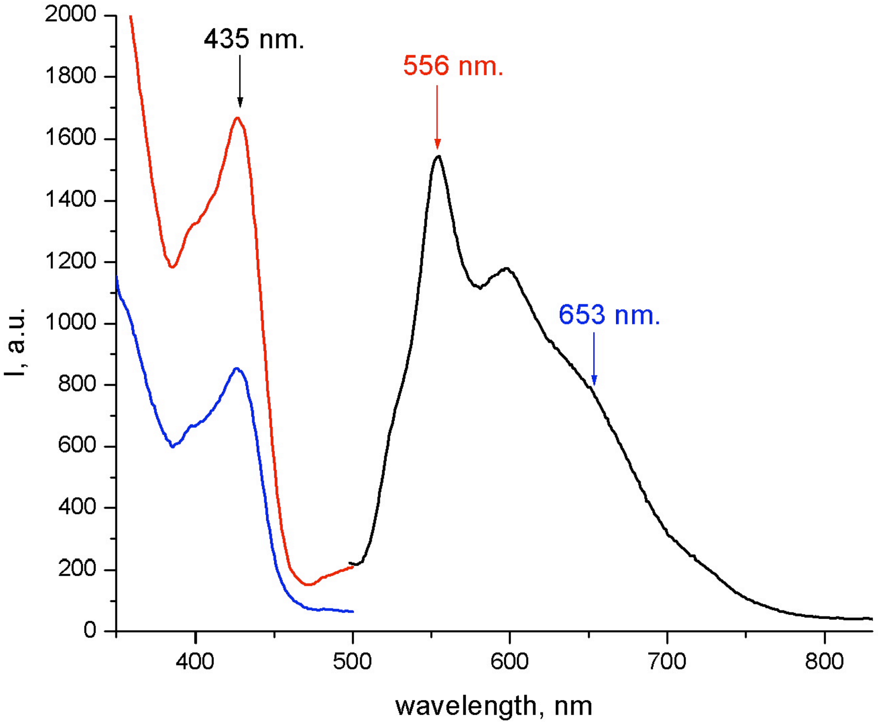
product was purified by column chromatography (silica gel, DCM/ethyl acetate 100/1, R*f* approx. 0.8) to give the required product. Yields were in the range of 45-60%. Yield 67%, δ_H ($CDCl_3$, 270 MHz): 0.89 (m, 18H), 1.3 (m, 24 H), 1.5 (m, 12H), 1.73 (m, 12H), 2.24 (4H, q, *J* = 7.3), 3.09 (4H, t, *J* = 7.3), 3.41 (4H, t, *J* = 7.3), 3.93 (t, *J* = 6.7 Hz, 8H), 3.94 (t, *J* = 6.7 Hz, 4H), 6.59 (s, 4H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 9.30 (s, 2H, $^3J_{HPt}$ 37.4 Hz). Other homologues were prepared in the same way.

Analytical data for platinum complexes **5**-*n* and **6**-*n*

	Calculated			Found		
	C	H	N	C	H	N
5-4	59.67	6.45	2.68	59.60	6.44	2.65
5-6	63.27	7.55	2.31	63.32	7.80	2.59
5-8	65.99	8.38	2.03	65.62	8.08	1.81
5-10	68.12	9.03	1.81	67.88	8.85	1.88
5-12	69.83	9.55	1.63	69.38	9.33	1.38
cyclopenteno						
6-6	64.92	7.71	2.16	64.76	7.65	2.13
6-10	69.19	9.08	1.72	69.11	9.03	1.69
6-12	70.73	9.58	1.56	70.45	9.51	1.68



Excitation (for the emission wavelength at 660 nm) and emission (excitation at 430 nm) spectra of pure film of **5**-6 obtained by spin coating of DCM solution (100 mg cm^{-3}) on a glass substrate.



Emission (black, excitation at 435 nm) and excitation (red for the emission wavelength at 556 nm and blue for the emission wavelength at 653 nm) spectra of pure film of **6**-6 obtained by spin coating of DCM solution (100 mg cm^{-3}) on glass substrate followed by heating at 110 °C for 10 min.

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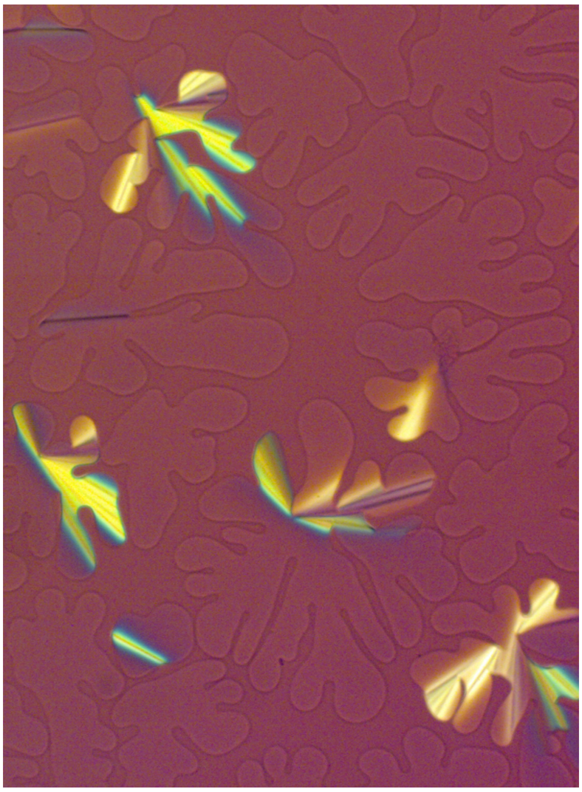
1 V.N. Kozhevnikov, D. N. Kozhevnikov, T. V. Nikitina, V. L. Rusinov, O. N. Chupakhin, M. Zabel, B. König, *J. Org. Chem.*, **2003**, *68*, 2882.

2 Pyridinium chloride is a classical reagent for cleavage of aryl methyl ethers at 200-220 °C avoiding strongly acidic or basic conditions. V. Prey, *Chem. Ber.*, **1942**, *75B*, 350.



Optical texture of **6**-10 taken at 230 °C on cooling from isotropic melt.

X-Ray Diffraction Data for **5**-10 and **6**-10

Compds	*T*/°C	d_{exp}/Å[a]	*I*[a]	[hkl][a]	d_{theo}/Å[a]	*Parameters*[a,d]
5-10	120	61.82 (sp)	S (sh)			
		32.34	S (sh)	11		a = 58.94 Å
		29.47	VS (sh)	20		b = 38.68 Å
		17.26	S (sh)	31	17.52	S = 2280 $Å^2$
		14.57	W (sh)	40	14.7	
		12.73	W (sh)	13	12.6	$\mathrm{Col_r}$-*c2mm*
		11.25	S (sh)	51	11.28	
		10.82	S (sh)	33	10.78	
		9.81	VW (sh)	60	9.82	
		9.65	M (sh)	04	9.7	
		8.65	M (sh)	53/62	8.7	
		8.23	M (sh)	71	8.22	
		7.98	W (sh)	44	8.1	
		7.06	W (sh)	73/64/35	7.05/6.9/7.2	
		6.55	M (sh)	55/06	6.47/6.45	
		6.21	W (sh)	26	6.29	
		4.7	S (br)			
		4.3	S (br)			
		3.4	S (br)			
	140	61.5 (sp)	S (sh)			
		32.11	S (sh)	11		a = 59.08 Å
		29.54	VS (sh)	20		b = 38.25 Å
		17.32	S (sh)	31	17.51	S = 2260 $Å^2$
		11.21	S (sh)	51	11.29	
		10.58	S (sh)	33	10.7	$\mathrm{Col_r}$-*c2mm*
		8.65	M (sh)	53/62	8.7	
		8.25	M (sh)	71	8.24	
		4.6	VS (br)			
		4.3	VS (br)			
		3.4	VS (br)			
6-10	180	77.0 (sp)	S (sh)			
		37.65	VS (sh)	10	37.63	a = 43.44
		21.72	VW (sh)	11	21.72	
		18.88	VW (sh)	20	18.81	$\mathrm{Col_h}$-*p6mm*
		14.21	M (sh)	21	14.22	
		12.57	M (sh)	30	12.54	
		10.87	S (sh)	22	10.86	
		10.42	S (sh)	31	10.44	
		9.4	M (sh)	40	9.41	
		8.61	M (sh)	32	8.63	
		8.21	M (sh)	41	8.21	
		4.7	S (br)			
		3.7	S (br)			

[a] d_{exp} and d_{theo} are the experimentally measured and theoretical diffraction spacings. The distances are given in Å; sp stands for superstructure. [b] Intensity of the reflections: VS: very strong, S: strong, M: medium, W: weak, VW: very weak; br and sh stand for broad and sharp reflections, respectively. [c] [*hk*] are the Miller indices of the reflections. [d] d_{theo} and the mesophases parameters *a*, *b*, *S,* are deduced from the following mathematical expressions. For the $\mathrm{Col_h}$ phase, the lattice parameter $a = 2[\Sigma_{hk}d_{hk}.(h^2+k^2+hk)^{½}]/\sqrt{3}N_{hk}$ where

N_{hk} is the number of *hk* reflections, and the lattice area (= columnar cross-section) $S = a^2 3^{1/2}/2$. For the Col$_r$ phase, $\langle d_{hk} \rangle = 1/[(h^2/a^2+k^2/b^2)^{½}]$, the lattice area $S = a \times b$ (columnar cross-sections = $S/2$). For columnar phases, it is practical to use the following relationships: $N = h.S/V_{mol}$; where N is the number of molecules (or molecular equivalents), V_{mol} is the molecular volume (estimated with a density close to 1) and h the average thickness of a disc or repeating stacking distance along the column, deduced directly from the X-ray pattern. Abbreviations: Col$_h$ = hexagonal columnar phase; Col$_r$ = rectangular columnar phase.

Image plate patterns for 5-10 at 140 °C (upper) and 120 °C (lower) obtained on cooling from the isotropic phase.

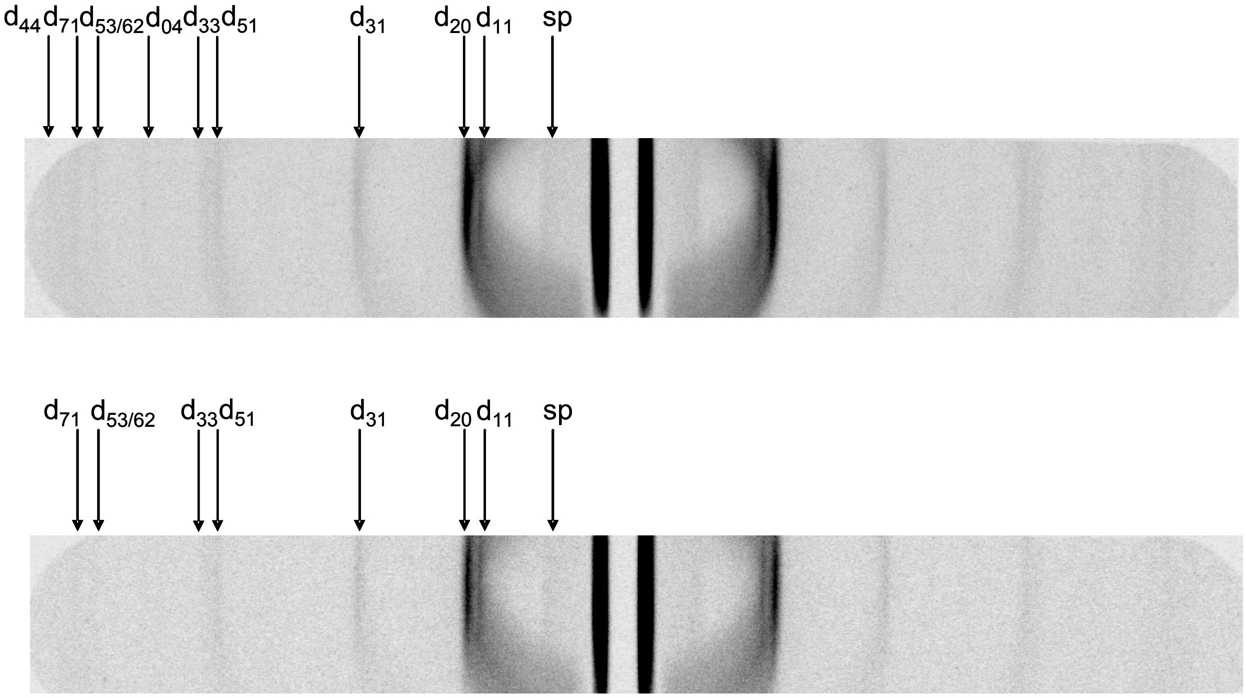
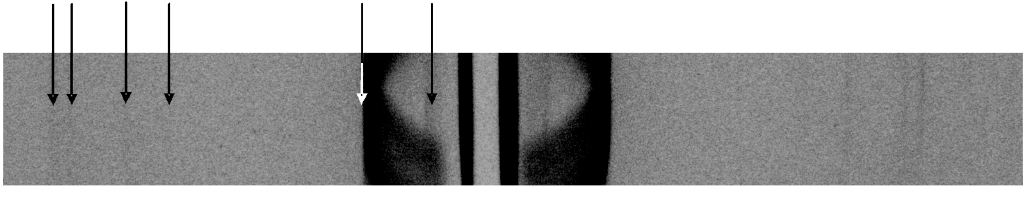


Image plate pattern for 6-10 at 180 °C obtained on cooling from the isotropic phase.



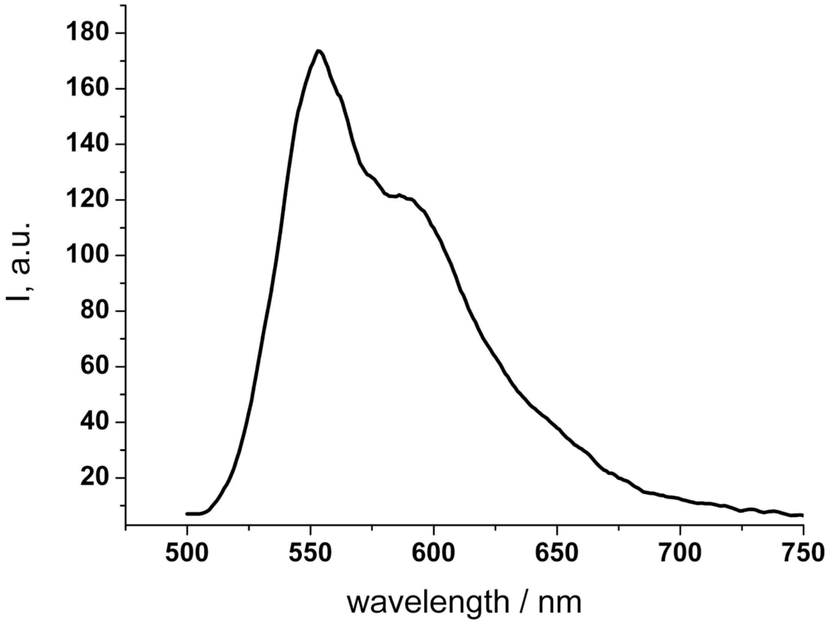
X-Ray data manipulation:

The relationship:

$$hS = NV$$

relates the number of molecules or molecular equivalents (N) in a slice of column that is h Å high to the volume of the molecule (V) and the cross-sectional area (S) of the column projected onto the basal plane. The relationship assumes unit density as written, although other densities can clearly be factored in.

Thus, for **5**-10, S (cross-sectional area of a column) is calculated as 1140 Å^2 and so if $h = 4.3$ Å and ρ is assumed to be 1 g cm^{-3}, then $N \approx 1.9$ ($V = 2600$ Å^3). However, there are two values for $d(001)$ plus a Pt$\cdots$Pt separation and so the choice of h may be slightly arbitrary. Thus, use of the formula must be taken both with this knowledge and with the knowledge that N does not need to take an integer value.



Emission spectrum of **5**-6 in CH_2Cl_2 at 10^{-5} mol dm^{-3} ($\lambda_{excitation}$ = 405 nm)