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PAPER

Photoconductive Nile red cyclopalladated metallomesogens†

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The synthesis and the electrochemical, photophysical and photoconductive properties of two new cyclometallated metallomesogens are described. These two complexes were respectively obtained by covalent metallation of Nile red, or a polyalkylated Nile red derivative, to a palladium(II) ion and by using a polyalkylated Schiff base as an ancillary ligand to complete the coordination sphere of the metal centre. The introduction of long alkyl chains on either one or both ligands leads to disk-shaped metallomesogens with ordered room temperature columnar organisation induced, in both cases, by the formation of dimeric pairs. As shown by powder X-Ray diffraction studies, both complexes exhibit a columnar rectangular mesophase over a wide temperature range. These complexes show a redox solution behaviour characterised by one reversible single-electron reduction and two consecutive reversible oxidation waves, which give them an electrochemical amphoteric character. Energy levels and distributions of frontier orbitals have been estimated. Photoconductivity of the mesophase at room temperature has been observed from UV-Vis to near IR wavelength. The high thermal, electrochemical and mesophase stabilities of the studied Nile red complexes confirm that cyclometallated Pd(II) complexes form a new class of photoconductors with features suitable for molecular semiconductor applications.

Introduction

In recent years, a rising interest in low-cost, flexible and easy to process electronic devices motivated the development of organic electronic technologies.¹ Applications of organic semiconducting materials include photodetectors, sensors, thin film transistors, lasers, and light emitting and photovoltaic devices.² Semiconductors, where charge carrier generation is promoted *in situ* by light absorption, are photoconductors.³ The photogeneration process at the origin of photoconductors or defect sites, or induced by doping) or intrinsic⁵ (when a charge-pair state is formed and after its dissociation the resulting holes/electrons can drift through the bulk material). The best photoconductors present high photogeneration efficiency as well as high charge mobilities. Over the last decade, discotic liquid crystals have received particular attention as semiconducting materials due to their columnar organisation which enhances charge mobility.⁶ Indeed, along the column stacks of discotics, charge mobilities several orders of magnitude higher than in other directions have been measured, and a hole mobility as high as $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has recently been reported for tri-indole-based discotic liquid crystals. This particularly high charge mobility was obtained by reducing the stacking distance between molecules and preserving a high intramolecular order along the columns.⁷

For most organic compounds, the photoconduction is limited by the low photogeneration efficiency. To overcome this limitation, organic devices must often be sensitized by incorporation of pigments such as phthalocyanines, squaraines, perylenes or azopigment derivatives, or by means of a double layer architecture where the photosensitizing layer is in contact with a transport layer.^{3,8} Another approach, which is yet to be developed but whose preliminary results are encouraging, is the use of photoconductive metallomesogens. Metallomesogens combine the properties of transition-metal centres with the self-organisation of the liquid crystalline state, hence high absorption properties at higher wavelength are expected, in contrast to fully organic liquid crystals. In this context we recently reported on a new class of photoconductive cyclometallated complexes. These complexes feature a 5-membered Pd(II) or Pt(II) metallocycle, obtained by using a H(C^N) cyclometalled ligand such as azobenzene H(Az), benzo[h]quinoline H(Bq) or 2-phenylpyridine H(Pp), and a 6membered metallocycle formed by a Schiff base H(O^N) ancillary ligand. Some of these complexes have shown excellent

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photorefractive properties either dispersed into a polymeric matrix⁹ or in their bulk amorphous state¹⁰ and their excellent photogeneration–photoconduction properties were recently correlated with their chemical structure.¹¹ In fact, the HOMO and LUMO distributions are separated by the metal centre, with the HOMO mainly localised onto the Schiff base moiety while the LUMO is mainly distributed onto the cyclometallated ligand. Moreover, theoretical computations have shown that the first singlet and triplet excited states exhibit a distorted geometry around the metal centre when compared to the ground state. Such distortion may further delay the return to the ground state of excited molecules, hence enhancing charge separation efficiency, leading to the excellent photoconductive behaviour observed for this new class of complexes (Chart 1).

As illustrated in Chart 2 (complexes I and II), by incorporating long alkyl chains at the periphery of both ligands, discotic mesophases were obtained.¹² Furthermore, by changing the chemical nature of the linker between the cyclometallated core and the alkyl chains (ester for I vs. ether for II), it was possible to tune the absorption properties of the resulting complexes and to obtain cyclopalladated liquid crystal complexes photoconductive at room temperature from UV-Vis to near IR (from 300 to 800 nm).¹² Due to their high viscosity, low mesophase temperature range (from room temperature to *ca*. 50 °C) and low degree of order of the columnar organisation, the photoconduction of these complexes could be, however, increased by only one order of magnitude upon thermal annealing, when compared to the same property in non-annealed samples.

In general, in order to improve both the stability and the degree of order of discotic mesophases, several approaches have been developed and are commonly used, such as (i) increasing the size of the discoid core,¹³ (ii) the introduction of secondary interactions such as hydrogen bonds,¹⁴ and (iii) the generation of helicoidal conformation that induce a higher degree of order.¹⁵ Taking advantage of such tools, a red luminescent cyclopalladated complex (Chart 2, complex **III**) exhibiting a columnar phase over a broad temperature range (35–173 °C) was recently obtained.¹⁶ This discotic mesogen was synthesized by cyclopalladation of the Nile red dye using a polyalkylated derivative of curcumin as an ancillary ligand.

In the present work we report the synthesis and characterisation of two new room temperature photoconductive discotic



Chart 1 Photoconductive cyclometallated complexes.



Chart 2 Photoconductive discotics (I, II) and luminescent discotic (III).

liquid crystals, obtained by using either Nile red or a polyalkylated Nile red derivative as cyclopalladated ligands and a polyalkylated Schiff base as an ancillary ligand. The incorporation of Nile red as a cyclometallated ligand has proven to maintain the physical separation of the frontier orbitals on their respective fragment, as shown by comparative cyclic voltammetry studies, leading to efficient photoconduction over a wide wavelength window. The Nile red fragment also induces, *via* formation of hydrogen bonded interactions through paired molecules, a wide temperature range of liquid-crystallinity with a high degree of order.

Results and discussion

Synthesis

The synthesis of both complexes IV and V (Scheme 1) was achieved in two steps through the formation of their corresponding palladium acetato-bridged intermediates (1 and 1' respectively) obtained by cyclometallation of either Nile red H(NR) or the Nile red derivative $H(NR)^1$ with palladium acetate, as previously described for the cyclometallation of H(NR).¹⁷ The bridge cleavage of 1 and 1' was performed using the Schiff base



Scheme 1 Experimental conditions: (i) acetic acid, 55 °C, 4 h; (ii) ethanol/dichloromethane, r.t., 5 days.



Scheme 2 Experimental conditions: (i) HCl, H_2O , 0-5 °C, 4 h; (ii) DMF, 70 °C, 8 h; (iii) K_2CO_3 , KI cat., DMF, 130 °C, 8 h.

 $H(O^N)^1$, prepared according to the previously reported procedure.¹²

H(NR) and its hydroxy-derivative **2** (Scheme 2) were prepared in two steps by slight modifications of previously reported syntheses.¹⁸⁻²⁰ Nitrosation of 3-diethylaminophenol gave a mixture of 5-diethylamino-2-nitrosophenol **3a** and its hydrochloride salt **3b** in a 1 : 2 ratio, as determined from the ¹H-NMR spectrum of the mixture. Since both **3a**²⁰ and **3b**¹⁹ have been successfully used in cycling reactions for obtaining Nile red derivatives, the mixture was used in the second step without any further purification. **H(NR)** and **2** were then obtained by reaction of **3a,b** with naphthol and 1,7-dihydroxynaphthalene, respectively. **H(NR)**¹ was finally obtained by etherification of **2** with 3,4,5-tris(dodeciloxy)bromomethylbenzene **4**.¹²

Complex (NR)Pd(BSC₆), analogous to the photoconductive complexes (C^N)Pd(BSC₆) (Chart 1), has been synthesised with the purpose of carrying out a complete electrochemical study and of determining the influence of the NR fragment onto the frontier orbitals of the resulting NR cyclometallated complexes. (NR) Pd(BSC₆) has been obtained through the rupture of the bridge intermediate 1 by the Schiff base H(BSC₆) following the pathway previously described for complexes IV and V.

Mesomorphic properties

At room temperature, the new cyclopalladated complexes IV and V are dark blue waxy solids. Their thermal behaviour was investigated by using polarized optical microscopy (POM), thermogravimetry (TGA) and differential scanning calorimetry (DSC). Both compounds, as observed by TGA, are thermally stable until 180 °C. While complex IV shows typical DSC diagrams of liquid crystalline phases through repetitive scans of heating–cooling cycles (Table 1, DSC traces are reported in the ESI†), for complex V no thermal transitions were observed by DSC, probably due to its high viscosity and a clearing point close to its decomposition temperature. It is noteworthy that for complex IV the DSC traces obtained on the third and successive

Table 1 Thermodynamic data for all thermal transitions observed by DSC for complex **IV** during 3 heating–cooling cycles (Col_r: columnar rectangular, I: isotropic liquid)

Complex	DSC scan	Transitional properties, T (°C), $[\Delta H$ in kJ mol ⁻¹]
IV	1 st heating 1 st cooling 2 nd heating 2 nd cooling 3 rd heating cycle	Waxy powder – 177 [72.6] – I I – 139 [29.5] – Col _r ' – 62 [11.0] – Col _r – 37 [3.6] – frozen Frozen – 33 [4.0] – Col _r ' – 77 [11.6] – Col _r – 160 [24.4] – I Identical data of the 1 st cooling Identical data of the 2 nd cycle

heating/cooling cycles are identical, indicative of the high stability and reversibility of the mesophases. The mesophases of complex **IV**, observed by POM upon slow cooling from the isotropic phase, show typical birefringent textures of liquid crystals but their identification was not possible for the absence of perceptible specific motifs.

Unequivocally, the mesophase determination was achieved by powder X-ray diffraction studies (PXRD) at variable temperatures. Both complexes **IV** and **V** present a columnar rectangular organisation (Colr). The indexations of the PXRD patterns and the cell parameters of complexes **IV** and **V** are presented in Table 2, together with the previously reported data of complexes **I–III**, for direct comparison.

While the substituted azobenzene cyclometallated fragment induced a hexagonal columnar mesophase for complexes I and II (Chart 1) over a very short range of temperature (from r.t. to *ca.* 50 °C), complexes III–V present a rectangular mesophase over a wide range of temperature up to 160–170 °C. Furthermore, the cell parameters and hence the cross-sections (S_r) of their mesophases are much larger than the average radius of the molecules (estimated at *ca.* 32 Å for IV, *ca.* 53 Å for V), as previously observed also for complex III, for which it was hypothesised on this basis the formation of a possible dimer constituting the mesophase.¹⁶ To further verify this hypothesis, the number of molecules by cell unit (*z*) for complexes II–V has been estimated according to eqn (1),²¹

$$Z = \frac{\rho \mathcal{N}_{\rm A} S_{\rm r} h}{M} \tag{1}$$

where ρ is the density of the liquid crystal phase, N_A is Avogadro's constant, S_r is the columnar cross-section, h is the height of the columnar unit cell and M is the molecular mass of the liquid crystal. S_r can be easily calculated from the cell parameters keeping in mind that its expression is dependent on the cell's geometry (see Table 3). The height of the columnar unit cell can be extracted from the PXRD pattern as the mean distance given by the halo in the wide angle attributed to intracolumnar stacking distance $(h = h_0)$. For the liquid crystal density some hypothesis has to be made. It is customary to consider a standard density of 1 g cm⁻³, a typical value for most organic phases.²² However, for discotic liquid crystals, density values are expected to be slightly higher. As an example, density values of *ca.* 1.1 g cm⁻³ have been reported for columnar hexaalkyloxytriphenylenes²³ and values up to 1.2 g cm⁻³ were recently adopted for some potassium salts of columnar crown ethers.24 A higher density than those encountered in common organic

Table 2	Indexations	of PXRD	spectra	of comp	olexes	I_V	V
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Complex	Temp.	$d_{ m obs}({ m \AA})$	hk	d_{calcd} (Å)	Mesophase and cell parameters ^{<i>a</i>}	Density ρ (g cm ⁻³)	Molecules number in unit cell (z)
I ¹²	r.t.	32.83	10	32.83	Col. n6mm		N.C. ^b
-		19.32	11	18.95	$a_{\rm h} = 37.9 \text{ Å}$		
		4.47	$h_{\rm ch}$		$S_{\rm r} = 1245 {\rm \AA}^2$		
\mathbf{H}^{12}	r.t.	31.07	10	31.07	$Col_h, p6mm$	1.2	0.98
		18.67	11	17.93	$a_{\rm h} = 35.9 \text{ Å}$		
		16.24	20	15.53	$\ddot{S_r} = 1115 \text{ Å}^2$		
		12.24	21	11.74	1		
		4.36	$h_{\rm ch}$				
		3.44	h_0^{ch}				
\mathbf{III}^{16}	140 °C	46.46	20	46.46	Col _r , c2mm	1.2	4.24
		38.57	11	38.57	$a_{\rm r} = 92.9 {\rm ~\AA}$		
	On second heating cycle	24.53	31	25.01	$\dot{b_r} = 42.4 \text{ Å}$		
	6.2	21.78	02	21.20	$\dot{S}_{\rm r} = 3939 \ {\rm \AA}^2$		
		14.07	13	13.97	1		
		12.83	33	12.86			
		4.56	$h_{\rm ch}$				
		3.39	h_0				
IV	125 °C	32.52	20	32.52	$Col_r, p2gg$	1.2	4.08
		18.62	02	18.62	$a_{\rm r} = 65.0 {\rm \AA}$		
		14.14	32	14.14	$b_{\rm r} = 37.2 {\rm ~\AA}$		
	On cooling from 160 °C	11.42	23	11.61	$a_{\rm r}/b_{\rm r} = \sqrt{3}$		
	e	9.17	14	9.22	$\dot{S}_{r} = 2421 \text{ Å}^{2}$		
		8.03	44	8.09	•		
		7.66	54	7.60			
		6.70	45	6.77			
		4.27	$h_{\rm ch}$				
		3.85	h_0				
V	r.t	35.81	20	35.81	Col _r , <i>c2mm</i>	1.2	3.84
	On cooling from 160 °C	21.19	02	21.19	$a_{\rm r} = 71.62 {\rm ~\AA}$		
	e	14.36	13	13.85	$b_{\rm r} = 42.38 {\rm ~\AA}$		
		12.53	33	12.15	$S_{\rm r} = 3035 \ {\rm \AA}^2$		
		7.28	55	7.29			
		4.42	$h_{\rm ch}$				
		4.03	h_0				
	70 °C	36.74			Highly disordered LC		
	On second heating cycle	14.42			-		
^a Calculate	d with $a_{\rm h} = 2d_{10}/\sqrt{3}$ (Col _b); and	nd $a_{\rm r} = 2d_{20}$,	$b_r = 2d_0$	2 (Col _r). ^b Not	t calculated in the absence of	of the h_0 signal.	
2010010100	= $10 v c (00 m)$, u		-1 -440	$_{2}$ (30.1). 100			

discotics is expected for complexes I–V, which contain a palladium metal centre. For this reason, a density value of $\rho = 1.2$ g cm⁻³ has been chosen for all complexes. Under these conditions, the unit cell of the Col_h mesophase of complex II turns out to be constituted of only one molecule. For complex I the number of molecules by cell unit cannot be determined, due to the higher disorder of its mesophase, resulting in the absence of the halo peak h_0 in the wide angle region of its PXRD pattern. For all Nile red metallomesogens, complexes III–V, Col_r mesophases have been obtained with a number of molecules by a unit cell of z = 4.

Considering the estimated indexations of their PXRD patterns (Table 2) together with the extinction rules,^{15c,25} the space groups of the mesophases have been determined to be *c2mm* for **III** and **V** and *p2gg* for **IV**. As evidenced in Table 3, for both these space groups the number of diskoids present in the cross-section is $Z_{\text{disk}} = 2$, which unequivocally implies that each disk is formed by two molecules, forming a dimer-like diskoid. In order to gain a deeper insight into the possible structure of these dimers, we have performed theoretical calculations on **H(NR)** molecules by molecular mechanics (Experimental section). The energy-minimised conformation of two drawn up **H(NR)** molecules converged to the geometrically highly stable optimized structure of a dimer presenting a 6-hydrogen-bond network, established

between two side-by-side molecules placed in a head-to-tail arrangement, which involves oxygen atoms and aromatic hydrogen atoms of the **H(NR)** molecules, as well as hydrogen atoms of the amino-alkyl chains, as shown in Fig. 1a. Consequently, the mesophases of the new complexes **IV** and **V** are constituted of full-disk shaped dimer structures, as represented in Fig. 1b. The formation of this dimer structure can explain the high thermal stability of the Col_r mesophase, which is maintained over a wide temperature range, as well as its higher degree of order when compared to the Col_h mesophases formed by complexes **I** and **II** (Chart 2).

Another important feature evidenced by the PXRD pattern is the higher order of the columnar mesophase of complex IV even at high temperatures, when compared with the rather disordered mesophase displayed by complex V, for which the indexation of the PXRD pattern was only possible at room temperature, in a frozen state. This drastic increment of disorder can easily be attributed to the additional alkyl-chains on the NR fragment, which probably sterically hinder the π - π stacking of adjacent disks that would promote a long-range order within the columns. It is noteworthy that this steric hindrance does not prevent the formation of the highly stable dimeric form of the complex through the hydrogen bonded network.



Table 3 Lattice structures of hexagonal and rectangular columnar liquid crystals with the corresponding cross-section area and the number of diskoids Z_{disk} (disk or ellipsoid) in the cross-section



Fig. 1 (a) Geometrically optimised structure of H(NR) dimer. Hydrogen bonds are represented by dashed lines (from 2.33 to 2.37 Å). (b) Scheme of resulting ellipsoid dimers IV and V.

Solution electrochemistry

Solution electrochemical data for complexes IV and V, obtained by cyclic voltammetry (CV), are collected in Table 4, together

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with the data of parent complexes $(C^N)Pd(BSC_6)$, $C^N = Az$, Bq, Pp (Chart 1) for direct comparisons.

Within the $(C^N)Pd(BSC_6)$ series, it can easily be noticed that regardless of the nature of the cyclometallated ligand (H(Az), H(Bq), H(Pp) or H(NR)), the HOMO energy value is maintained at ca. 5.4 eV. In contrast, the LUMO energy is highly dependent on the cyclometallated ligand, varying from 2.6 to 3.6 eV. This observation is consistent with the separation between HOMO and LUMO, the HOMO being localised onto the Schiff base fragment while the LUMO is mainly localised onto the cyclometallated fragment, as previously described and confirmed in the case of complexes (Az)Pd(O^N), (Bq)Pd(O^N) and (Pp) Pd(O^N) by theoretical calculations.¹¹ The incorporation of Nile red as a cyclometallated ligand therefore seems to maintain this separation. The cyclic voltammograms of complexes IV and V are reported in Fig. 2. Both complexes show a one electron reduction wave and two consecutive one-electron oxidation waves. Complexes IV and V show an identical reduction potential as their analogue (NR)Pd(BSC₆) but present a lower oxidation potential which is slightly decreased (by ca. 300 mV). This suggests that the addition of supplementary alkyl chains onto the Schiff base ligand allows a fine tuning of the HOMO energy level, lowering it, while the introduction of alkyl chains through an ether linkage onto the NR fragment does not modify the LUMO energy. Furthermore, while the first oxidation for complexes IV and V occurs at the same potential (+300 mV vs. Fc/Fc^+), the second oxidation for complex V occurs at a lower potential, reducing the gap between the two oxidation waves

 Table 4
 Cyclic voltammetry data^a

Compound	E^{red} (V) vs. Fc/Fc ⁺	E^{ox} (V) vs. Fc/Fc	Estimated LUMO (eV)	Estimated HOMO (eV)
(Az)Pd(BSC ₆) ¹¹	-1.48 (Rev.)	+0.78 (Irr.)	-3.3	-5.6
$(Ba)Pd(BSC_6)^{11}$	-2.23 (Irr.)	+0.57 (Irr.)	-2.6	-5.4
$(\mathbf{Pp})\mathbf{Pd}(\mathbf{BSC}_6)^{11}$	-2.43 (Irr.)	+0.61 (Irr.)	-2.4	-5.4
(NR)Pd(BSC ₆)	-1.20 (Rev.)	+0.60 (Irr.)	-3.6	-5.4
ĪV	-1.20 (Rev.)	+0.30 (Rev.)	-3.6	-5.1
V	-1.20 (Rev.)	+0.30 (Rev.)	-3.6	-5.1
^{<i>a</i>} Potentials are given	versus ferrocene/ferrocenium (F	c/Fc ⁺) (Rev.: reversible wave,	Irr.: irreversible wave).	



Fig. 2 Cyclic voltammograms of complexes IV (a) and V (b) in the presence of *ca.* 1 eq. of ferrocene as an internal reference (Fc/Fc⁺). Scan rate: 100 mV s⁻¹, DCM, Bu_4NPF_6 (0.1 M).

 $(E_2^{\text{ox}} - E_1^{\text{ox}} = 300 \text{ mV} \text{ for } IV, E_2^{\text{ox}} - E_1^{\text{ox}} = 200 \text{ mV} \text{ for } V)$. This oxidation behaviour suggests that the HOMO + 1 might be localised onto the **NR** fragment and that its energy is stabilised by the ether-linked alkyl chains. It is noteworthy that all redox processes for complexes IV and V are fully reversible, indicative of their high electrochemical stabilities.

UV/Vis spectroscopy and photoconduction

UV-Vis spectra of metallomesogens IV and V were obtained in dichloromethane solution, and data are reported in Table 5. The absorption properties of both complexes IV and V are spread on a wide wavelength window. In contrast to complex III,²⁶ no emission was observed, and both complexes do not show the solvatochromic properties of H(NR).²⁷

Both complexes IV and V, however, show photoconductive properties, *i.e.* an increase in electrical conductivity when exposed to light. A typical current increase under light
 Table 5
 Absorption maxima recorded in dichloromethane solution at room temperature

Complex	$\lambda/\text{nm} (\log \varepsilon)$
IV	259 (3.79), 306 (3.45), 334*, 373*, 437 (3.01), 570*, 608 (3.59)
V	254 (3.81), 302*, 352 (3.39), 377*, 573*, 609 (3.44)

irradiation is shown in Fig. 3 for complex IV, where the light was turned on at t = 2.5 s and turned off at t = 17.5 s.

Fig. 4 shows the photoconductivity of complexes IV and V versus the applied electric field E, normalized over the absorption coefficient α and the light intensity I. For complex V, it was not



Fig. 3 Current measured on a sample of IV exposed to light at $\lambda = 560$ nm under an applied electric field $E = 23 \text{ V } \mu \text{m}^{-1}$.



Fig. 4 Photoconductivities normalized over the absorption coefficient α and the light intensity *I* are reported for **IV** and **V**. The experiments were performed at $\lambda = 520$ nm and $I = 5 \times 10^{-3}$ W cm⁻² for **IV** and at $\lambda = 633$ nm and I = 2 W cm⁻² for **V**, while the absorption coefficients were 5213 cm⁻¹ for **IV** and 112 cm⁻¹ for **V**. The inset shows the photoconductivity of **IV** normalized over light intensity only.

possible to acquire data with an applied field higher than 7–8 V μ m⁻¹ because of dielectric breakdown at higher fields. It is clear that the photoconductivity of **IV** is about 1 order of magnitude higher than in **V**. This difference could be explained by considering that the stacking distance of **IV** is shorter than in **V** (3.85 Å *vs.* 4.03 Å). In addition, and perhaps more importantly, **IV** exhibits a higher long range order within the columns. It is well known that in discotic liquid crystals both a long range order and a short stacking distance increase the π -orbitals overlap between neighbouring molecules in the columns, favouring one-directional charge transport. This can increase charge mobility and photoconductivity even by several orders of magnitude.²⁸

The data reported in the inset of Fig. 4 show that the σ/I value for IV is in the order of 3×10^{-8} S cm W⁻¹ at 25 V µm⁻¹, which is a very high value when compared to the photoconductivity of other organic photoconductors,²⁹ especially because this result is obtained without addition of dopants and without any annealing process to increase the order. This result represents a tremendous step forward in the development of this class of photoconductors since in previously analyzed cyclopalladated complexes, at the same applied electric field, the σ/I value was of the order of 10^{-12} S cm W⁻¹ for annealed cyclopalladated discotics (complexes I and II),¹² while it was of *ca.* 10^{-9} S cm W⁻¹ for crystalline samples of the (C^N)Pd(O^N) series reported in Chart 1.¹¹

The wavelength dependence of the normalized photocurrent and of the absorption coefficient of complex **IV** is reported in Fig. 5. For photoconduction measurements, a particular cell geometry (Experimental section) has been used, allowing the observation of the photocurrent even for high values of absorption coefficients and for wavelengths well below the absorption limit of the ITO covered glass substrates. The observed photocurrent is proportional to the absorption of the material. In particular, it is noteworthy that how even a little decrease in the absorption between 300 nm and 330 nm results in a corresponding decrease in the photocurrent. Such behaviour was also observed for complex **V**. These new complexes show, therefore, photoconductive properties on a quite wide range of wavelength from below 200 nm up to 800 nm.

Photoconductivity was also measured as a function of the intensity of light. As shown in Fig. 6, it can clearly be deduced that the photocurrent varies with the square root of the light

60

50

40

30

20

10

0

200

_{photo} / I _{liaht} (a.u.)



500

600

λ (nm)

700

800

900

400

300



Fig. 6 Photocurrent *versus* light intensity for IV. Measurements were performed at $\lambda = 520$ nm with an applied field E = 16 V μ m⁻¹.

intensity. This can be explained by assuming that the carrier kinetics is controlled by a bi-molecular recombination process.³⁰

The extended absorption window coupled with their photoconductive properties render such Nile red metallomesogens potential candidates for many optoelectronic applications, particularly in photovoltaics where such features are important, a field in which organic discotics have recently proven to boost the power conversion efficiencies of devices.³¹

Conclusions

Absorption (a.u.

Two Nile red H(NR) cyclopalladated complexes exhibiting a columnar rectangular mesophase in a wide temperature range were synthesized. The mesophases were obtained by the selfassembly of ellipsoidal dimeric pairs kept together by a hydrogen bonding network. This particular dimer interaction lends a high stability to the mesophase and, in the case of complex IV, also a high order. The additional introduction of alkyl chains onto the **NR** fragment (complex V) does not prevent the formation of these dimeric pairs but dramatically increases the columnar disorder by steric hindrance. Both metallomesogens have shown an amphoteric redox behavior with fully reversible oxidation and reduction processes, showing their high electrochemical stabilities. Through the electrochemical estimation of the energy levels of their frontier orbitals, we have shown that HOMO and LUMO are physically separated by the palladium metal centre, the HOMO being mainly distributed onto the Schiff base ancillary ligand while the LUMO is mainly localized onto the cyclometallated Nile red fragment. A band-gap of ca. 1.5 eV imparts to these complexes a wide range window of absorption from the UV-Vis up to the near IR region, while the HOMO/LUMO physical separation probably originates their excellent photoconduction properties. Photoconductivity measurements, performed with a cell geometry that allows the observation of photocurrent even at low wavelengths, have shown the correlation between the absorption of the complexes and its photocurrent, with normalized photocurrent values reaching 3×10^{-8} S cm W⁻¹ at an applied electric field E = 25 V μ m⁻¹. All together, the features displayed by these new metallomesogens constitute highly significant improvements towards the use of such complexes in optoelectronic devices.

Experimental

General methods and procedures

All commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification. I.R. spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. ¹H-NMR spectra were recorded on a Bruker WH-300 spectrometer in deuterated solvents with TMS as an internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer CHNS/O. The powder X-Ray diffraction patterns were obtained by using a Bruker AXS General Area Detector Diffraction System (D8 Discover with GADDS) with Cu-K α radiation; the area detector was placed at a distance of 20 cm from the sample and at an angle $2\theta_D$ of 14°. Measurements were performed by charging samples in Lindemann capillary tubes with inner diameters of 0.5 mm. A CalCTec (Italy) heating stage was used to heat the samples at a rate of 5°C min⁻¹ to the appropriate temperature.

Electrochemical studies

All potentials were measured with IR compensation using an Epsilon electrochemical analyser. Voltammetry experiments were performed in a 3 mL cell of dry, freshly distilled, and degassed (N₂) dichloromethane solution using tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte, a Pt disk working electrode, a Pt wire counter-electrode and an Ag wire as a pseudo-reference electrode. Voltammograms were recorded at a 100 mV s⁻¹ scan rate from *ca*. 10^{-3} M complex solution. Redox potentials are given relative to a ferrocene/ ferrocenium (Fc/Fc⁺) redox couple used as an internal reference. Estimation of HOMO/LUMO energy values was performed taking into account -4.8 eV for Fc/Fc⁺.³²

Synthesis

5-Diethylamino-2-nitrosophenol (3a) and 5-diethylamino-2nitrosophenol hydrochloride (3b). 3-Diethylaminophenol (12.02 g, 72.6 mmol) was dissolved in a mixture of 26 mL of HCl and 16 mL of distilled water. The obtained solution was cooled to 0 °C under stirring and an aqueous solution of NaNO₂ (5.01 g, 72.6 mmol) was added. The reaction mixture was stirred for 4 h at 0– 5 °C. The precipitated solid was filtered, dried under vacuum and dissolved in hot ethanol (200 mL). After addition of diethylether (200 mL) and 24 h in the freezer, a mixture of **3a** and **3b** (in 1 : 2 molar ratio) was obtained as a brown-yellow crystalline powder (11.79 g), identified by comparison with NMR samples of pure compounds.^{19,20} Since either compounds have been already successfully used in cycling reactions for obtaining Nile red derivatives,^{19,20} the product was used without any further purification.

3a + *3b*: ¹H NMR (300 MHz, DMSO, 25 °C, TMS): δ = 7.53 (d, *J* = 10.65 Hz, 1H, **3b**), 7.26 (d, *J* = 10.3 Hz, 0.5H, **3a**), 7.19 (dd, *J* = 9.18 Hz, *J* = 2.2 Hz, 1H, **3b**), 6.83 (dd, *J* = 10.1 Hz, *J* = 2.4 Hz, 0.5H, **3a**), 6.54 (d, *J* = 2.6 Hz, 1H, **3b**), 5.7 (d, *J* = 2.6 Hz, 0.5H, **3a**), 3.7–3.3 (m, 6H, **3a** + **3b**), 1.25 (t, *J* = 7.3 Hz, 6H, **3b**), 1.16 (t, *J* = 7.4 Hz, 3H, **3a**); FT-IR (KBr, cm⁻¹): 3424 (*br*), 2979, 2755, 1626, 1545, 1491, 1146, 1040, 857, 749. Synthesis of H(NR). 1-Hydroxynaphthalene (1.00 g, 6.9 mmol) and the mixture **3a,b** (1.5 g, *ca.* 6.9 mmol) were dissolved in *ca.* 40 mL of dimethylformamide and the resulting solution heated at 70 °C for 8 h. The solvent was evaporated under reduced pressure and the crude solid purified by column chromatography (silica gel, dichloromethane/diethylether: 2/1).

H(NR): dark red solid; yield 23% (505 mg); m. p. 211 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.66$ (d, J = 7.69, 1H), 8.32 (d, J = 7.26, 1H), 7.74–7.59 (m, 3H), 6.66 (dd, J = 5.5Hz, J = 2.15 Hz, 1H), 6.46–6.44 (m, 1H), 6.38 (s, 1H), 3.46 (q, J =6.1 Hz, 4H), 1.28 (t, J = 11.9 Hz, 6H); FT-IR (KBr, cm⁻¹): 2964, 2935, 1624, 1584, 1555, 1403, 1306, 1255, 1111, 1020, 843, 778; elemental analysis: calcd (%) for C₂₀H₁₈N₂O₂ (318.14): C 75.45, H 5.70, N 8.80; found C 75.42, H 5.73, N 8.80.

Synthesis of 2. 1,7-Dihydroxynaphthalene (1.243 g, 7.5 mmol) and the mixture of 3a,b (1.580 g, *ca.* 7.1 mmol) were solubilized in *ca.* 40 mL of dimethylformamide and the resulting solution heated at 70 °C for 8 h. The solvent was evaporated under reduced pressure and the crude solid purified by column chromatography (silica gel, ethyl acetate/ethanol: 1/1).

2: green solid; yield 53% (1.327 g); m. p. 250 °C; ¹H NMR (300 MHz, DMSO, 25 °C, TMS): $\delta = 10.38$ (s, 1H), 8.57 (d, J = 9 Hz, 1H), 8.40 (d, J = 8.79 Hz, 1H), 7.43 (d, J = 2.58 Hz, 1H), 7.21 (d, J = 2.55 Hz, 1H), 7.18 (d, J = 2.58 Hz, 1H), 6.51 (d, J = 2.8 Hz, 1H), 6.02 (s, 1H), 3.44 (q, J = 7 Hz, 4H), 1.28 (t, J = 7.2 Hz, 6H); FT-IR (KBr, cm⁻¹): 3145 (*br*), 2971, 2920, 1635, 1584, 1559, 1328, 1114, 832, 518; elemental analysis: calcd (%) for C₂₀H₁₈N₂O₃ (334.13): C 71.84, H 5.43, N 8.38; found C 71.85, H 5.43, N 8.37.

Synthesis of $H(NR)^1$. 2 (276 mg, 0.83 mmol) was solubilized in 30 mL of DMF. To the obtained solution were added 1.5 eq. of K_2CO_3 (171 mg, 1.25 mmol) and a catalytic amount of KI. The reaction mixture was stirred for 10 min and 1 eq. of 4 (598 mg, 0.83 mmol) was added. The solution was heated at 130 °C for 8 h. The solvent was removed under reduced pressure and the product purified by column chromatography (silica gel, petroleum ether (b.p. 40–60 °C)/diethylether: 1/1).

H(NR)^{*I*}: red solid; yield 53% (428 mg); m.p. 113 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.60$ (d, J = 8.8 Hz, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.62 (d, J = 9.1 Hz, 1H), 7.36 (dd, J =8.8 Hz, J = 2.55 Hz, 1H), 6.71 (d, J = 2.55 Hz, 1H), 6.67 (d, J =4.4 Hz, 2H), 6.51 (d, J = 2.6 Hz, 1H), 6.42 (s, 1H), 5.11 (s, 2H), 3.97 (m, 6H), 3.48 (q, J = 7 Hz, 4H), 1.82–1.47 (m, 60H), 1.20 (m, 6H), 0.9–0.85 (m, 9H); FT-IR (KBr, cm⁻¹): 2928, 2848, 1624, 1588, 1559, 1332, 1259, 1122, 844; elemental analysis: calcd (%) for C₆₃H₉₆N₂O₆ (976.73): C 77.41, H 9. 09, N 2.87; found C 77.40, H 9.91, N 2.90.

Synthesis of acetato-bridged intermediate complexes 1'. The intermediate complex 1' was synthesized according to the previously reported procedure for 1 (ref. 16) with the following modifications: $H(NR)^1$ (187 mg, 0.2 mmol) was solubilized in 60 mL of acetic acid and 10 mL of dichloromethane. The resulting solution was heated at 55 °C for 6 days and filtered on Celite. The obtained solid was washed with acetonitrile.

I': dark-blue solid; yield 75% (161 mg); m.p. 154 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.74$ (d, J = 9.5 Hz, 1H), 7.0

(d, J = 2.5 Hz, 1H), 6.50 (s, 2H), 6.40 (d, J = 1.8 Hz, 1H), 6.35 (dd, J = 9.5 Hz, J = 2.9 Hz, 1H), 6.21 (d, J = 2.2 Hz, 1H), 6.03 (s, 1H), 4.69 (s, 2H), 4.1–3.8 (m, 6H), 3.3–3.1 (m, 4H), 2.31 (s, 3H), 1.9–1.6 (m, 6H), 1.5–1.4 (m, 6H), 1.4–1.1 (m, 54H), 0.9–0.8 (m, 9H); FT-IR (KBr, cm⁻¹): 2920, 2853, 1636, 1575, 1234, 1117, 1075, 720; elemental analysis: calcd (%) for C₁₃₀H₁₉₈N₄O₁₆Pd₂ (2283.29): C 68.31, H 8.73, N 2.45 found C 68.34, H 8.70, N 2.45.

Synthesis of complex IV. Intermediate 1 (100 mg, 0.10 mmol) and 1.5 eq. of $H(O^N)^1$ (ref. 12) (190 mg, 0.15 mmol) were solubilized in dichloromethane and ethanol and the reaction mixture was stirred at room temperature for 5 d. The solvent was removed under reduced pressure, and the resulting solid was washed with acetonitrile and precipitated from ethanol/ dichloromethane, filtered and reprecipitated from diethylether/ dichloromethane, filtered, washed with diethylether and with hot ethanol to yield a dark-blue solid.

IV: dark-blue waxy solid; yield 83% (211 mg); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 9.35$ (d, J = 9.51 Hz, 1H), 7.98 (s, 1H), 7.66 (d, J = 4.65 Hz, 1H), 7.41–7.39 (m, 1H), 7.38 (d, J = 8.07 Hz, 1H), 6.89–6.87 (m, 1H), 6.58 (s, 2H), 6.51 (d, J = 2.94 Hz, 1H), 6.36 (s, 1H), 6.28 (s, 1H), 6.23 (d, J = 8.07 Hz, 1H), 4.90 (s, 1H), 4.0–3.9 (m, 10H), 3.52 (q, J = 6.72 Hz, 4H), 1.9–1.7 (m, 10H), 1.6–1.2 (m, 96H), 0.95–0.81 (m, 15H); FT-IR (KBr, cm⁻¹): 2920, 2853, 1635, 1624, 1580, 1234, 1118, 1075, 720; elemental analysis: calcd (%) for C₁₀₀H₁₅₃N₃O₉Pd (1646.06): C 72.89, H 9.36, N 2.55; found C 72.90, H 9.38, N 2.56.

Synthesis of complex V. Intermediate 1' (161 mg, 0.07 mmol) and 2 eq. of $H(O^N)^1$ (ref. 12) (176 mg, 0.14 mmol) were dissolved in 30 mL of dichloromethane and 10 mL of ethanol. The reaction mixture was stirred at r.t. for 5 days. The solvent was removed under reduced pressure and the resulting solid was filtered and washed with hot ethanol, immediately filtered on a cotton filter and dissolved in dichloromethane.

V: dark-blue waxy solid; yield 67% (222 mg); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 9.28$ (d, J = 9.54 Hz, 1H), 7.94 (s, 1H), 7.55–7.39 (m, 2H), 7.04–6.78 (m, 4H), 6.7–6.4 (m, 6H), 6.36 (s, 1H), 6.26 (s, 1H), 5.92 (s, 1H), 4.85 (s, 2H), 4.47 (s, 2H), 4.12–3.71 (m, 16H), 3.5–3.6 (m, 4H), 2.2–1 (m, 190H), 0.1–0.8 (m, 15H); FT-IR (KBr, cm⁻¹): 2913, 2852, 1624, 1581, 1234, 1117, 720; elemental analysis: calcd (%) for C₁₄₃H₂₃₁N₃O₁₃Pd (2304.65): C 74.64, H 10.09, N 1.82; found C 74.61, H 10.12, N 1.62.

Molecular modelling

The **H(NR)** dimer structure was modelled and optimised in the gas phase using the Polak–Ribiere conjugate gradient method of the Hyperchem 7.51 programme (Hyperchem, Hypercube Inc., 1115 NW 4th street, Gainsville FL 32601, USA) following standard techniques.³³

Photoconductivity experiments

The substrates used to prepare the samples were obtained from Indium Tin Oxide (ITO) covered glass sheets (UNAXIS, 110 nm ITO thickness, sheet resistivity 12 $\Omega \Box^{-1}$). A photolithographic process was applied in order to pattern the ITO in 2 mm wide



Fig. 7 Side view of a sample (not in scale).

stripes. Patterned glasses were again covered with positive photoresist and each ITO stripe was exposed to light through a 2 mm long slit with an opening of 5 μ m or 10 μ m. By choosing the right process parameters, it was possible to remove the ITO from the glass in the exposed region, obtaining two ITO electrodes with sharp edges, as shown in Fig. 7. The span between the electrodes can be modulated by changing the slit width and the exposition time. Electrode separations in the 5–40 μ m range were obtained. The last step of the process was the spin-coating of the material, dissolved in chloroform with a typical concentration of 10 mg mL⁻¹. The thickness of the materials and the spacing between the electrodes were measured by using a Dektak 8 profilometer from Veeco.

Samples were then used to perform photoconductivity measurement. Note that by using the geometry shown in Fig. 7 and irradiating the sample from the top, light reaches the material under investigation directly, making it possible to perform photoconductivity experiments even at wavelengths below 350 nm, where ITO starts to absorb.

Photoconductivity experiments were performed by using either light from a Xe-Lamp/Monochromator system or from a He–Ne laser. To change the light intensity, a set of neutral density filters with different transmittance were used. The photocurrent i_{photo} was obtained from the difference between the dark and the light currents, measured using an electrometer (6517A from Keithley), also used to apply the electric field.

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