Not only columns: high hole mobility in a discotic nematic mesophase formed by metal-containing porphyrin-core dendrimers

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Abstract: We report a new family of multifunctional liquid crystalline porphyrin-core dendrimers which have coumarin functional groups around the porphyrin core. Porphyrin metalation strongly affects the photophysical properties, and therefore Zn (II) and Cu (II) derivatives have also been prepared. All synthesized dendrimers show nematic discotic mesophase. Their high tendency to homeotropic alignment makes these dendrimers excellent candidates for device applications due to their easy processability, spontaneous alignment between electrodes, self-healing of defects owing to their dynamic nature. The charge mobility values of these materials are the highest ever reported for a nematic discotic phase. Moreover, these values are similar to the highest values reported for ordered columnar mesophases and this shows that a supramolecular organization in columns is not necessary to achieve high charge mobility.

Organic electronic devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaic devices (OPVs), are based on the transport of electrical charges between electrodes.[1] The intrinsic supramolecular organization of Liquid Crystals (LC) is an effective asset that has been exploited in the preparation of such devices[2] and there are two reasons for this. On the one hand, the organization allows the control of order and packing, an important feature since charge transport in molecular materials is known to improve with orientational order. Furthermore, when compared to true 3-D solids, the incomplete positional order in LC systems means that they have a lower tendency to form structural defects and multi-domains on length-scales of the order of those needed in most devices. It is therefore not surprising that charge mobility has been studied most extensively in those LC phases that exhibit higher order. Smectic phases, in which roughly rod-shaped molecules are organized with a common average direction of their long axes within the structural motif of layers, show relatively high mobilities, usually within the 10^{-4}–10^{-1} cm^{2}V^{-1}s^{-1} range.[3] As with all LC properties, such mobility is highly anisotropic, with the highest values in directions within the layer plane, since the combination of molecular structure and order within the phase favors π-π intermolecular interactions within the plane. The same interactions are invoked to explain the high mobilities of columnar phases, which are formed by stacked, disk-shaped molecules that typically consist of a rigid central aromatic core surrounded by several flexible alkyl chains. The combination of π-π interactions between the central rigid cores and of the conformational freedom of the external chains, which allows space-filling and favors molecular mobility, frequently leads to columnar organizations.[4] In such phases charge mobilities of the order of 1 cm^{2}V^{-1}s^{-1} along the direction of the columns have been reported. However, columnar mesophases still suffer from the disadvantage that orientationally uniform domains that are large enough to be used in most devices are often hard to obtain, even with the help of long thermal annealing, surface treatments or complex processing techniques.[5] In the work reported here it was found that charge mobilities of the same order of magnitude as those recorded in columnar phases can also be obtained in Nematic Discotic (N_D) mesophases where, due to the lower degree of order, large uniform domains are achievable relatively easily. In contrast to the columnar phases, where the disk-shaped molecules are stacked in long columns, which in turn form rectangular or hexagonal lattices, N_D phases do not have long-range positional order but only orientational order, where molecules share a common average orientation of the normal to the central rigid cores.[6] The N_D phase is far less common than columnar phases and in this work the N_D phase was obtained by exploiting the porphyrin a core in a newly synthesized dendrimeric structure.

The materials used in this work consist of a porphyrin central core covalently linked to four dendronic structures derived from a 3,4,5-trialkoxycarboxylic acid bearing coumarin moieties (**Figure 1**). The porphyrin core has often been used as a central platform to obtain discotic LC materials[7] and it is also relevant for organic electronic applications due to their photostability, photoabsorption over a broad range of wavelengths, interesting photophysical properties and convenient chemical synthesis.[8] In addition, porphyrin metalation has a marked effect on the photophysical properties and therefore the Cu(II) and the Zn(II) derivatives were also prepared. Coumarin units have been used in plastic electronics or light and energy harvesting[9] and these act as

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fluorophores that modify the physical properties of these supermolecular systems.

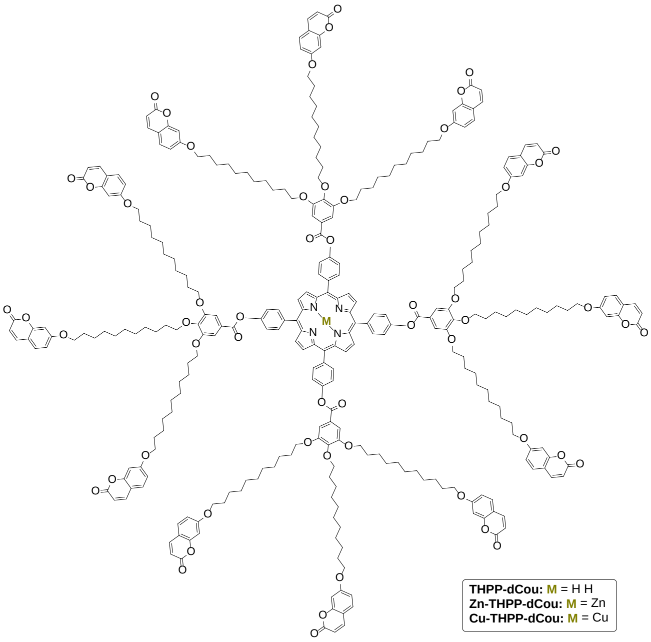

Figure 1. Chemical structure of the porphyrin-core dendrimers.

The synthesis of the the porphyrin-core dendrimers was described in the Supporting Information. The chemical structures of all the compounds were confirmed by IR spectroscopy, one-dimensional ^{1}H and ^{13}C NMR spectroscopy (**Figure S1-S6**) and two-dimensional ^{1}H-^{1}H COSY, DOSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments, MALDI-TOF mass spectroscopy (**Figure S7-S8**) and elemental analysis.

The thermal stability of the three compounds was studied by thermogravimetric analysis (TGA) using powdered samples. All of the samples showed good thermal stability and in all cases the 2% weight loss temperature ($T_{2\%}$) was detected above the clearing point (**Table 1**).

Table 1. Thermal properties.

	$T_{2\%}$ [ºC][a]	T_{onset} [ºC][b]	Phase transitions[c]
THPP-dCou	232	409	g 16 N_D 61 I[d]
Zn-THPP-dCou	271	403	g 11 N_D 74 I[d]
Cu-THPP-dCou	215	402	g 17 N_D 73 I[d]

[a] Temperature at which 2% mass loss is detected in the thermogravimetric curve. [b] Onset temperature associated with mass loss detected in the thermogravimetric curve. [c] DSC data of the second heating process at a rate of 10 ºC min^{-1}. g: glass, N_D: nematic discotic mesophase, I: isotropic liquid. [d] POM data.

Thermal transitions and mesomorphic properties were studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) and the results are listed in **Table 1**. The DSC curves (**Figure 2a**) of the free base and metal porphyrin-core dendrimers show only a glass transition freezing of the mesomorphic order at room temperature. The clearing temperatures were established by POM observations because transition peaks were not detected in the DSC curves. All of the compounds displayed enantiotropic liquid crystalline mesophases from room temperature. Due to their tendency to homeotropic alignment, the mesophase was observed by POM on applying mechanical stress to the samples (**Figure 2b** and **Figure S9**). The incorporation of Zn^{2+} and Cu^{2+} metal ions into the porphyrins enhances the thermal stability of mesophases and their clearing temperatures are raised by 10–15 ºC. The enhanced interactions between neighboring porphyrins is believed to be responsible for this improvement, as metalation has been shown to increase both the rigidity of the porphyrin rings and their electrostatic attraction.[7a, 7d]

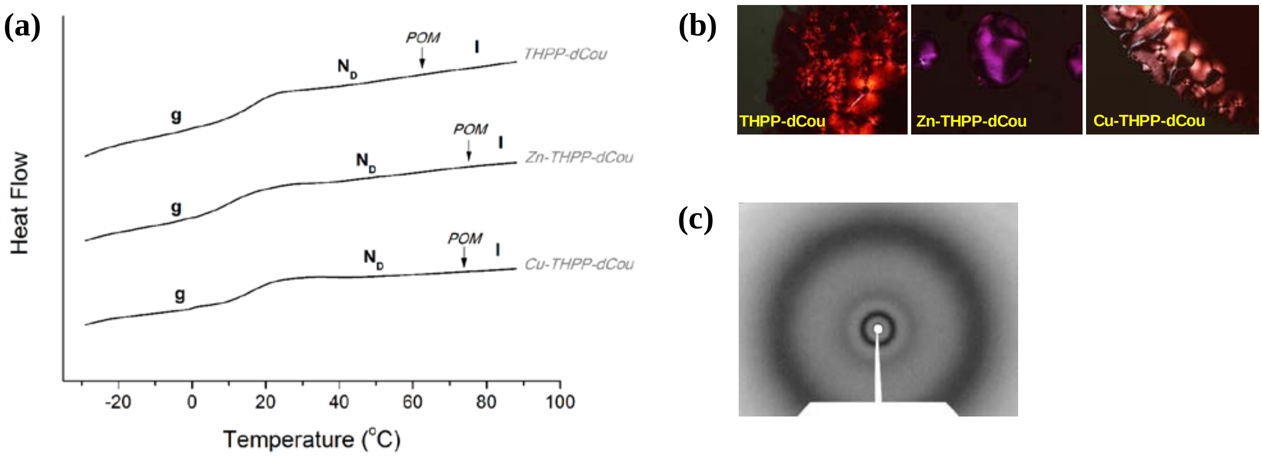

Figure 2. (a) DSC traces corresponding to the second heating scan for the porphyrin-core dendrimers (10 ºC min^{-1}, Exo down). (b) POM microphotographs observed in the cooling process at room temperature after applying mechanical stress. (c) Room temperature XRD patterns of Cu-THPP-dCou in the N_D mesophase.

The nature of the mesophase was identified by XRD. The diffractograms recorded for all porphyrin-core dendrimers showed only diffuse scattering in the low-angle region (**Figure 2c**) due to the lateral disk-disk distance. In the high-angle region a broad diffuse halo was observed and this is related to the conformational disorder of the liquid-like hydrocarbon chains. These patterns, along with the POM textures shown in **Figure 2b**, are consistent with a nematic discotic (N_D) mesophase, which has only orientational order.[10] Indeed, the absence of Bragg reflections and the presence of only diffuse reflections indicate that there is no periodical order and thus the presence of columnar structures can be ruled out.

The UV-Vis absorption and fluorescence spectra of the porphyrin-core dendrimers were recorded on dilute solutions (10^{-5} to 10^{-7} M) in dichloromethane (DCM) and in thin films at room temperature (**Figures S10-S13**). Relevant data are listed in **Table S1**.

The absorption and fluorescence spectra for the components **dCou** and **THPP** are shown in **Figure S14**. There is partial overlap of the **THPP** absorption spectrum (λ_{abs} = 420 nm) and **dCou** emission spectrum (λ_{em} = 388 nm). In the present porphyrin-core dendrimers, the porphyrin unit serves as an acceptor whereas multiple coumarin donors are present in the dendrimer periphery. When coumarin donors were excited selectively (λ_{exc} = 320 nm), emission from both the coumarin units and the porphyrin acceptor was observed, thus demonstrating that fluorescence resonance energy-transfer (FRET) was facile but not quantitative in these systems (**Figure S13**). Intramolecular energy transfer occurs from coumarin moieties to the porphyrin core (antenna effect), despite the low degree of overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor (**Figure S14**). FRET efficiencies (Φ_{FRET}) were calculated by comparing the donor emission in the presence of the acceptor relative to that in the absence of the acceptor[11] and moderate Φ_{FRET} values were obtained.

The fluorescence spectra at an excitation wavelength of λ_{exc} = 320 nm were also recorded in thin film and compared to the data from DCM solutions and almost no residual emission of the coumarin moieties was observed (**Figure S15**). This finding demonstrates that FRET from coumarin units to the porphyrin core is more efficient in the thin film than in DCM solution. This behavior is probably because in the solid state the porphyrin-core dendrimers are in the N_D mesophase and this forces the porphyrin ring to be in the same plane as the coumarin units, with this arrangement leading to enhanced electronic communication.[12]

In order to investigate the feasibility of electron and hole injection processes in these new porphyrin-core dendrimers, cyclic voltammetry (CV) measurements were carried out. The voltammograms are presented in **Figure S16**. All of the porphyrin-core dendrimers exhibit similar cyclic voltammograms and these compounds can be easily oxidized. However, meaningful reduction processes were not detected. The HOMO and LUMO energy levels referred to the vacuum level were estimated by combining electrochemical and optical data. The values are summarized in **Table 2**.

The charge carrier mobilities of the porphyrin-core dendrimers were measured by the space charge-limited current (SCLC) technique. SCLC was chosen considering the HOMO energy value of the materials, which matches the work function of Au and thus ensures the formation of an ohmic contact. The SCLC measurements were carried out in films placed between Au- and ITO-coated glass electrodes, as described in the Supporting Information.

A typical double logarithmic plot of the current density (*J*) versus applied voltage (*V*) is shown in **Figure 3a**. All materials showed ohmic behavior at low voltages with a typical linear relationship. At higher voltages, where the current becomes space-charge-limited, a quadratic relationship was observed. In the SCLC region the mobility could be calculated from the modified Mott–Gurney equation:[13]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_0 \exp\left(\beta\sqrt{\frac{V}{d}}\right)\frac{V^2}{d^3} \qquad (1)$$

in which *J* is the measured current density, μ_0 is the zero-field charge mobility, ε_0 is the free-space permittivity, ε_r is the relative dielectric constant of the material, *V* is the applied voltage, *d* is the thickness of the device and β is a constant that describes the field dependence of the mobility. Within this model, the mobility is expressed as:[14]

$$\mu = \mu_0 exp\left(\beta\sqrt{\frac{V}{d}}\right) \qquad (2)$$

Table 2. Electrochemical parameters and hole mobilities at room temperature.

	E_{ox} [V][a]	E_{HOMO} [eV][b]	λ_{edge} [nm][c]	ΔE_g [eV][d]	E_{LUMO} [eV][e]	μ_{0hole} [cm^{2}V^{-1}s^{-1}]	$\beta/10^{-2}$ [cm$^{0.5}$V$^{-0.5}$]	$\mu_{hole(at\ E=5\ V/\mu m)}$ [cm^{2}V^{-1}s^{-1}]
THPP-dCou	0.94	–5.26	592.0	2.09	–3.17	$5\cdot10^{-10}$	2.5	1.2 10^{-7}
Zn-THPP-dCou	0.61	–4.93	554.5	2.24	–2.69	0.12	1.0	1.1
Cu-THPP-dCou	0.88	–5.20	545.7	2.27	–2.93	0.03	1.1	0.34

[a] Onset potential for the first oxidation process. [b] E_{HOMO} = – (E_{ox} – $E_{1/2,\ FOC}$ + 4.8) *eV*. [c] Intersection of the normalized UV-Vis absorption spectrum and the fluorescence spectrum. [d] Optical band gap, calculated by $\Delta E_g = hc/\lambda_{edge}$. [e] E_{LUMO} = E_{HOMO} + ΔE_g

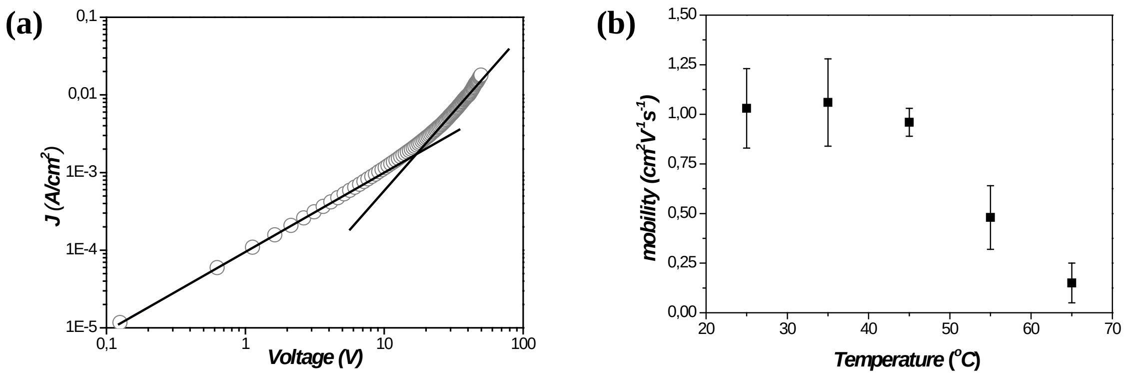

Figure 3. (a) Typical current/applied voltage curve for a 8.8 µm thick **Cu-THPP-dCou** (symbols represent experimental data and the two continuous lines represent the ideal linear and quadratic dependence of J on V). (b) Temperature dependence of mobility for a 9.3 µm thick sample of **Cu-THPP-dCou**. These data are taken over the best performing area of the sample.

and the two parameters μ_0 and β can be extracted from fittings of the SCLC sections of the experimental data. The resulting hole transport mobilities are summarized in **Table 2**. The effect of the presence of the metal on charge mobility is dramatic and it can be appreciated on comparing the mobilities of the compounds at an applied field E = 5 V/μm within the range of the SCLC sections of the experimental J-V curves. In fact, while the free porphyrin derivative shows a very low μ_{hole} value (1.2 10^{-7} cm^{2}V^{-1}s^{-1}), the metal-porphyrin derivatives exhibit a hole mobility 6–7 orders of magnitude higher. Regardless of the presence of the metal, these porphyrin-core dendrimers showed a strong tendency to orient with their short molecular axes normal to the substrate: without any surface treatment the alignment of the director was perfectly homeotropic for all compounds (director normal to the plane of the substrates; dark view observed by POM between crossed polarizers). This situation rules out the possibility that the large difference in mobility associated with metalation is due to a difference in macroscopic orientational order. The hole mobility of **Cu-THPP-dCou** was also measured at different temperatures. The mobility gradually decreased with increasing temperature as the isotropic transition was approached (**Figure 3b**). An SCLC regime was not observed when experiments were performed on the isotropic phase. To our knowledge, the hole mobility values measured for these metal porphyrin-core dendrimers are the highest ever reported for nematic discotic phases.[15] In fact, the values of the charge carrier mobility obtained for **Zn-THPP-dCou** and **Cu-THPP-dCou** are comparable to the highest values described to date in the more ordered hexagonal columnar mesophases.[16] In columnar phases, the high mobility values are commonly rationalized in terms of the high charge transfer rates allowed within the stack by the π-π intermolecular interactions between the cores of neighboring molecules. However, the phase structure of the N_D phase does not exhibit any long-range columnar order and this leaves an open question as to why such a high mobility is observed in the N_D phases formed by **Zn-THPP-dCou** and **Cu-THPP-dCou** that, given the information outlined above, must be connected with metalation. A certain degree of short-range columnar order cannot be excluded but, given the lack of influence of metalation on the XRD patterns, a direct influence of metalation on the orientational properties can be excluded. It seems more reasonable to invoke either or both of (a) a direct involvement of the metal in the charge transfer via metal-metal or metal-nitrogen intermolecular interactions and (b) an increase in the transfer integral due to the metal-induced variation of the ring shape, leading to stronger intermolecular interactions, as also suggested by the increase in the clearing temperature with metalation. The decisive influence that metalation has on the physical properties of some liquid crystal derivatives has been reported in previous works, although in many cases it is not possible to propose a plausible explanation for the experimental results.[4e, 17] The data presented in this work do not allow further conclusions to be drawn regarding this important issue and more experimental and theoretical investigations are required.

In conclusion, we have prepared a new family of disc-like liquid crystalline dendrimers with a porphyrin core and luminescent coumarin units at the periphery. All of the porphyrin-core dendrimers studied display a nematic discotic (N_D) mesophase and are stable up to 200 ºC. It has also been demonstrated that excitation of the coumarin moieties leads to energy transfer to the luminescent porphyrin core. Despite the fact that the compounds exhibit a nematic discotic phase, the charge mobility values measured in the metal-porphyrin derivatives are among the highest reported for discotic mesogens to date, including the values observed in the much more ordered columnar phases. In their N_D phases, the studied compounds show a high tendency to form large homogeneously oriented domains, with very low levels of defects and scattering losses, as observed by POM. In addition, the compounds have a high viscosity and good processability and, in this respect, they are quite similar to thermoplastic polymers. For the reasons outlined above, the results described in this work seem to open a new way to the design of organic materials for optoelectronic applications.

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[1] a) T. W. Kelley, P. F. Baude, C. Gerlach, D. E. Ender, D. Muyres, M. A. Haase, D. E. Vogel, S. D. Theiss, *Chem. Mater.* **2004**, *16*, 4413; b) A. W. Hains, Z. Liang, M. A. Woodhouse, B. A. Gregg, *Chem. Rev.* **2010**, *110*, 6689; c) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595; d) T. M. Figuera-Duarte, K. Müllen, *Chem. Rev.* **2011**, *111*, 7260. e) M. Gsänger, D. Bialas, L. Huang, M. Stolte, F. Würthner, *Adv. Mater.* **2016**, *28*, 3615;

[2] a) W. Pisula, M. Zorn, J. Y. Chang, K. Müllen, R. Zentel, *Macromol. Rapid Commun.* **2009**, *30*, 1179; b) M. O'Neill, S. M. Kelly, *Adv. Mater.* **2011**, *23*, 566; c) E.-K. Fleischmann, R. Zentel, *Angew. Chem. Int. Ed.* **2013**, *52*, 8810.

[3] a) J.-i. Hanna, A. Ohno, H. Iino, *Thin Solid Films* **2014**, *554*, 58; b) H. Iino, T. Usui, J.-i. Hanna, *Nat. Commun.* **2015**, *6*, 6828.

[4] a) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902; b) B. R. Kaafarani, *Chem. Mater.* **2011**, *23*, 378; c) T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, *Chem. Rev.* **2016**, *116*, 1139; d) S. Kumar, *Chemistry of discotic liquid crystals: from monomers to polymers*, CRC Press, Boca Raton 2011.

[5] a) A. M. van de Craats, N. Stutzmann, O. Bunk, M. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzy, H. Sirringhaus, R. H. Friend, *Adv. Mater.* **2003**, *15*, 495; b) W. Pisula, Ž. Tomović, M. Stepputat, U. Kolb, T. Pakula, K. Müllen, *Chem. Mater.* **2005**, *17*, 2641; c) I. O. Shklyarevskiy, P. Jonkheijm, N. Stutzmann, D. Wasserberg, H. J. Wondergem, P. C. M. Christianen, A. P. H. J. Schenning, D. M. de Leeuw, Ž. Tomović, J. Wu, K. Müllen, J. C. Maan, *J. Am. Chem. Soc.* **2005**, *127*, 16233; d) W. Pisula, X. Feng, K. Müllen, *Chem. Mater.* **2011**, *23*, 554.

[6] H. K. Bisoyi, S. Kumar, *Chem. Soc. Rev.* **2010**, *39*, 264.

[7] a) A. Segade, M. Castella, F. López-Calahorra, D. Velasco, *Chem. Mater.* **2005**, *17*, 5366; b) T. Sakurai, K. Shi, H. Sato, K. Tashiro, A. Osuka, A. Saeki, S. Seki, S. Tagawa, S. Sasaki, H. Masunaga, K. Osaka, M. Takata, T. Aida, *J. Am. Chem. Soc.* **2008**, *130*, 13812; c) S. Sengupta, S. Uemura, S. Patwardhan, V. Huber, F. C. Grozema, L. D. A. Siebbeles, U. Baumeister, F. Würthner, *Chem. Eur. J.* **2011**, *17*, 5300; d) M. Salamończyk, D. Pociecha, A. Nowak-Król, D. Koszelewski, D. T. Gryko, E. Górecka, *Chem. Eur. J.* **2015**, *21*, 7384; e) B. Wu, K. Chen, Y. Deng, J. Chen, C. Liu, R. Cheng, D. Chen, *Chem. Eur. J.* **2015**, *21*, 3671.

[8] a) C. M. Drain, A. Varotto, I. Radivojevic, *Chem. Rev.* **2009**, *109*, 1630; b) I. Beletskaya, V. S. Tyurin, A. Y. Tsivadze, R. Guilard, C. Stern, *Chem. Rev.* **2009**, *109*, 1659; c) W.-S. Li, T. Aida, *Chem. Rev.* **2009**, *109*, 6047; d) M. Urbani, M. Grätzel, M. K. Nazeeruddin, T. Torres, *Chem. Rev.* **2014**, *114*, 12330.

[9] S. R. Trenor, A. R. Shultz, B. J. Love, T. E. Long, *Chem. Rev.* **2004**, *104*, 3059.

[10] a) P. H. J. Kouwer, W. F. Jager, W. J. Mijs, S. J. Picken, *Macromolecules* **2001**, *34*, 7582; b) P. H. J. Kouwer, W. F. Jager, W. J. Mijs, S. J. Picken, *Macromolecules* **2002**, *35*, 4322.

[11] a) S. L. Gilat, A. Adronov, J. M. J. Fréchet, *Angew. Chem. Int. Ed.* **1999**, *38*, 1422; b) A. Adronov, S. L. Gilat, J. M. J. Fréchet, K. Ohta, F. V. R. Neuwahl, G. R. Fleming, *J. Am. Chem. Soc.* **2000**, *122*, 1175; c) S. Hecht, N. Vladimirov, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2001**, *123*, 18.

[12] a) B. Jiang, S.-W. Yang, W. E. Jones, *Chem. Mater.* **1997**, *9*, 2031; b) M. Mao, Q.-H. Song, *Dyes Pigm.* **2012**, *92*, 975.

[13] P. N. Murgatroyd, *J. Phys. D: Appl. Phys.* **1970**, *3*, 151.

[14] P. M. Borsenberger, L. Pautmeier, H. Bässler, *J. Chem. Phys.* **1991**, *94*, 5447.

[15] M. Inoue, H. Monobe, M. Ukon, V. F. Petrov, T. Watanabe, A. Kumano, Y. Shimizu, *Opto-Electron. Rev.* **2005**, *13*, 303.

[16] a) E. M. García-Frutos, U. K. Pandey, R. Termine, A. Omenat, J. Barberá, J. L. Serrano, A. Golemme, B. Gómez-Lor, *Angew. Chem. Int. Ed.* **2011**, *50*, 7399; b) A. Benito-Hernández, U. K. Pandey, E. Cavero, R. Termine, E. M. García-Frutos, J. L. Serrano, A. Golemme, B. Gómez-Lor, *Chem. Mater.* **2013**, *25*, 117

[17] a) J. L. Serrano, *Metallomesogens : synthesis, properties, and applications*, VCH, Weinheim; New York 1996; b) N. Hoshino, *Coordination Chemistry Reviews* **1998**, *174*, 77; c) S. Collinson, D. Bruce, in *Transition Metals in Supramolecular Chemistry,* Vol. 5 (Ed: J. P. Sauvage) John Wiley & Sons, Ltd, **1999**, 285., 2007, 285; d) A. S. Mocanu, M. Amela-Cortes, Y. Molard, V. Circu, S. Cordier, *Chem. Commun.* **2011**, *47*, 2056.

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