Invited Paper

Functionalized Porphyrin Discotic Liquid Crystals: Photoinduced Charge Separation and Trapping[1]

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Individual members of a family of highly absorptive porphyrins bearing symmetrically positioned flexible side chains form discotic liquid crystalline mesophases at modest temperature ranges. The order of this phase is preserved when a thin layer of this self-assembled material is cooled to room temperature. Exposure of such films to visible excitation, with or without an externally applied electrical field, produces photovoltaic effects and/or charge trapping. The latter effect constitutes the basis for optoelectronic information storage.

INTRODUCTION

Many of the applications of new photonic and optoelectronic materials[2-4] require that the compound or polymer of interest be positioned in a highly regular spatial arrangement, preferably within a thin film. A straightforward corollary of this requirement is that if it were possible to attain the regular spacing afforded by crystal packing forces in an organic thin film, many interesting materials properties could be probed. Although it is clearly possible to formulate crystallographically ordered polymers as a thin film,[5] general routes for the preparation of films of varying thickness are rare and their execution requires exceptional dedication and skill.

An alternative approach to the preparation of ordered thin films is to employ compounds of low or medium molecular weight that can self-assemble. Organized molecular assemblies within lipid bilayers play an important role in photosynthesis,[6] and a series of very interesting artificial systems based on covalent or non-covalent associations between the ordered material and a support have been developed within the last several years.[7] Among various self-assembling molecules, liquid crystals are a unique subset whose properties can range from surfactant-like aggregates to rigid rod-like arrays to disc-like stacks.[8,9] The spontaneous order achieved in the liquid crystalline phase is often rapidly restored by "self-healing", if disturbed by some external perturbation. This spontaneous restoration of order is both common and essential to normal function in biological systems, and analogous features can be highly useful for practical applications of artificially designed ordered materials. For example, a self-healing system can obviate order

defects in a way that is difficult to attain in solid crystals, and films with this property can be recovered more easily (by a heating-cooling cycle) from otherwise fatal fracture that might take place during practical operation of a device containing the material of interest.

Our interests have focussed on discotic liquid crystals, a family of coin-shaped materials that tend to align along their short axes, in one of the several conceivable arrangements shown in Fig. 1.[10] Two types of anisotropic fluids are possible: (1) stacked (columnar) arrays which differ in the
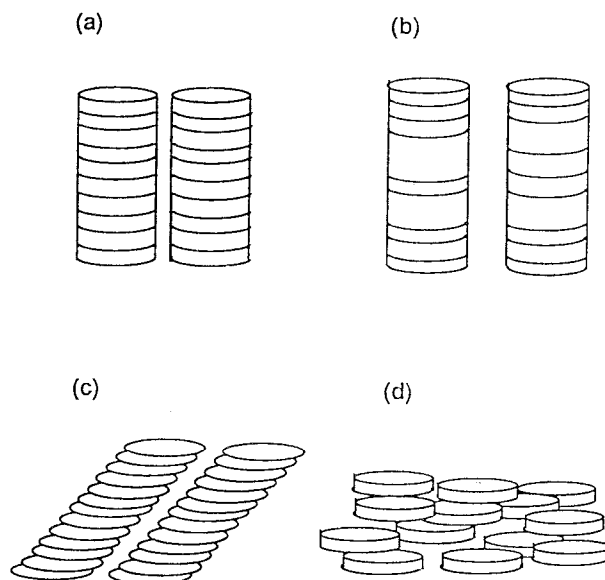

Fig. 1. Simple representations of possible stacking interactions in discotic liquid crystals: (a) - (c) columnar phases and (d) a nematic phase.[10]

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degree of fixed order along the axis, and (2) scattered (nematic) phases that align parallel, but not in stacks. Most of the constituent molecules of discotic liquid crystals have molecular structures with a near planar aromatic core, symmetrically surrounded by long, conformationally flexible alkyl, alkoxy, or ester chains,[8] usually with six or more atoms in the attached chains.[11] The preferred alignment is thought to derive from a balance between steric interactions between the appended chains and π, π interactions along the stacked cores. Various columnar discotic mesophases can also be differentiated by viewing along the two dimensional columnar lattice as shown in Fig. 2.[12] The physical characteristics that lead to a preference for one arrangement over another are not yet understood.

The first reported discotic liquid crystal, a benzene-hexa-n-alkanoate, was described in 1977.[8] Its lowest energy absorption maximum lies within the ultraviolet region of the spectrum, making it difficult to study when dispersed as a thin film on conventional optically transparent (metal oxide) semiconductor surfaces. The first porphyrinic liquid crystal was synthesized by Goodby and coworkers in 1980 by

esterifying the acetic and propionic acid side chains of uroporphyrin I with dodecanol.[10] Soon thereafter a liquid crystalline phthalocyanine was prepared and its discotic order described.[13] Unfortunately, this liquid crystalline phthalocyanine showed no isotropic phase below 300 °C, making it difficult to formulate as a thin film by standard methods. Lower temperatures for the transitions to and from the discotic mesophase could be achieved with a liquid crystalline porphyrin 1, synthesized in Austin in 1989,[14] than could be attained with this phthalocyanine. Subsequent investigation showed 1a (M = Zn, R = n-C$_8$H$_{17}$) to have interesting solid-state photophysical properties[15] and significant photoconductivity, making it useful for photovoltaic applications.[16,17]

(a) Hexagonal
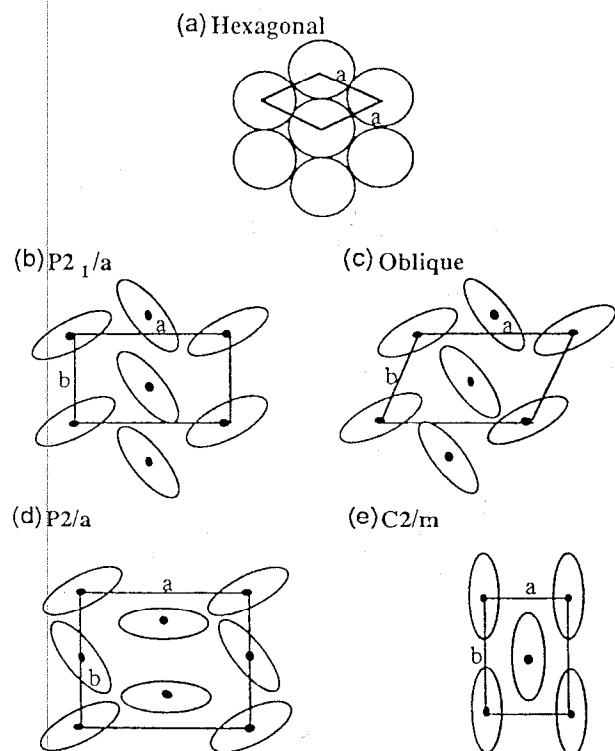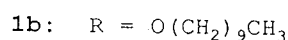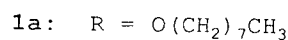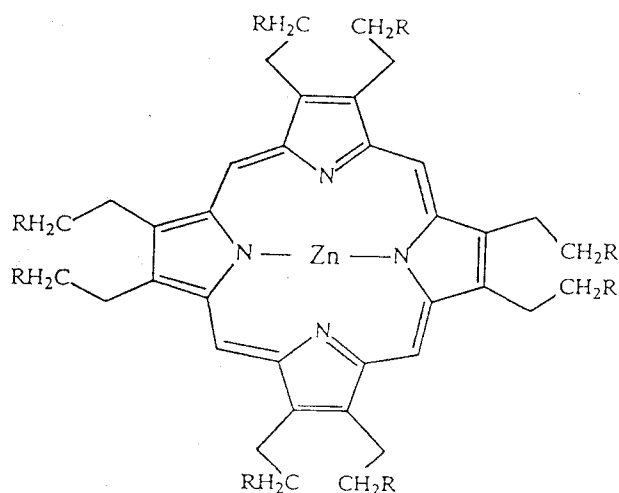
(b) P2$_1$/a

(c) Oblique

(d) P2/a

(e) C2/m

Fig. 2. Possible orientations of columnar discotic mesophases viewed from a two-dimensional lattice. Circles are used to denote planes normal to the columnar axis and ovals are used to denote tilted phases.[9]

1a: R = O(CH$_2$)$_7$CH$_3$

1b: R = O(CH$_2$)$_9$CH$_3$

We have therefore studied analogous members of the family 1 with regard to their molecular structures, focussing on 1b (M = Zn, R = C$_{10}$H$_{21}$) as a model. We have also probed the mechanism of charge separation in oriented, solid thin films of 1a and 1b with the goal of probing its utility as a light-absorbing self-assembling material in molecular electronic and optical devices. This article contains a brief review of our reported progress toward this objective.

RESULTS AND DISCUSSION

Synthesis and Characterization of 1

The synthesis of 1 was accomplished by the acid-catalyzed condensation of 3,4-bis(alkoxymethyl)pyrrole. The preparation of this functionalized pyrrole was accomplished through known routes, as outlined in Fig. 3.[14,15] Metallation

was accomplished by heating a hot dimethylformamide solution of the crude porphyrin under reflux for 15 min. in the presence of excess solid $Zn(OAc)_2$. Phase transition temperatures for the metallated porphyrins were determined by differential scanning calorimetry (dsc) and by monitoring light transmission changes with a polarizing microscope equipped with a calibrated hot stage. The stability of **1** from room temperature to about 350 °C in air was established by the invariance of the dsc trace upon repeated heating and cooling cycles. Compound **1a** has a solid-to-columnar discotic liquid crystal phase transition (10.8 kcal/mol) at 107 °C and a discotic-to-isotropic transition (5.9 kcal/mol) at 162 °C; for **1b**, these same transitions occurred at 86 °C (14.9 kcal/mole) and 142 °C (5.2 kcal/mol). The assignment of the liquid crystalline phase as a columnar discotic phase was based on low angle X-ray scattering measurements[1] and the full miscibility of **1a** and **1b** with a columnar discotic phthalocyanine.[13]

The spectral characteristics of **1** were typical of a func-

tionalized porphyrin.[14] In particular, the absorption spectra of **1**, when measured in dilute solution, exhibited a strong Soret band at about 400 nm and two weaker Q bands, responsible for their intense red color, at 540 and 570 nm.[16] The Soret band was blue-shifted and the Q bands red-shifted upon aggregation, with discrete exciton bands appearing in the region from 420 to 500 nm upon preparing an amorphous film by evaporative removal of solvent from the dilute solution. Spectral resolution in this region was improved by heating to the liquid crystalline phase, allowing the film to reorder and self-heal, before cooling again to room temperature, where the other spectral measurements were made. The quantum yield for fluorescence in the solid film was found to increase with increasing order and becomes wavelength-dependent, possibly because of an enhanced probability of ring-to-ring charge transfer through the π-stacked array. Fluorescence from the ordered film was temperature-dependent, with significant changes in fluorescence intensity being observed at the phase transition temperatures.
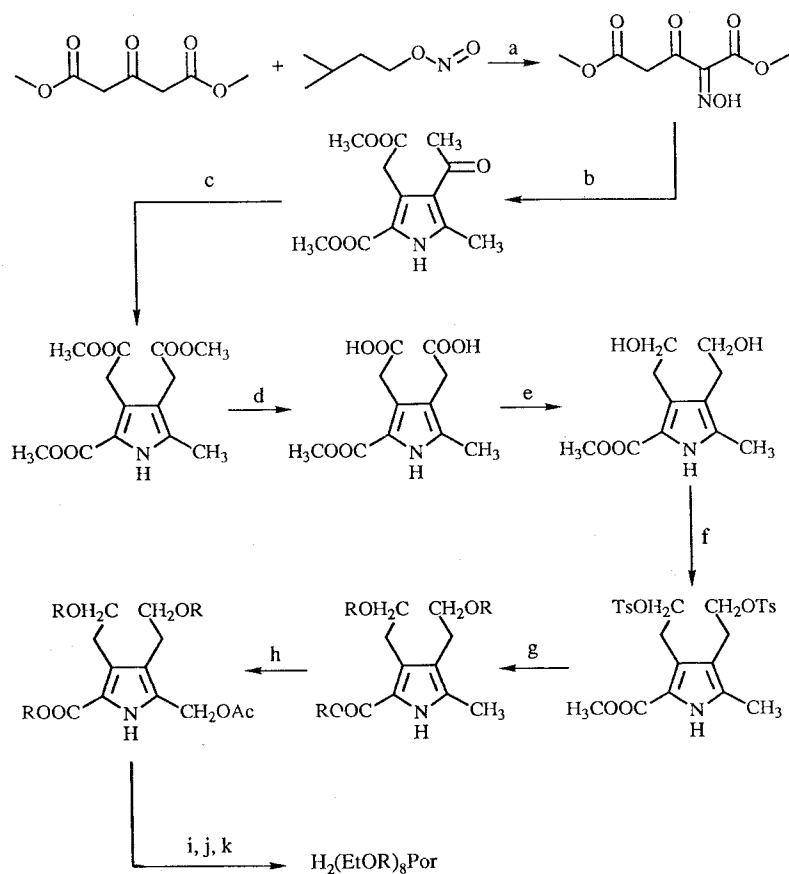

Fig. 3. Synthesis of Liquid Crystalline Porphyrins **1**.[14] Reagents employed in these conversions: (a) HCl; (b) 2,4-pentanedione/Zn/HOAc/75 °C; (c) $Tl(NO_3)_3$/MeOH/HClO₄; (d) NaOMe/MeOH; (e) BH₃/THF; (f) TsCl/pyridine; (g) ROH/toluene; (h) Pb(OAc)₄; (i) KOH/EtOH; (k) chloranil.

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Fabrication of Ordered Thin Films from 1

Thin films of porphyrin **1** were prepared by capillary filling of the isotropic melt into a sandwich cell constructed from two optically transparent indium tin oxide (ITO) electrodes separated by a polymer spacer of defined thickness (typically 0.5 to 5 μm), Fig. 4.[17] By slowing cooling the melted liquid through the liquid crystalline phase, the film was allowed to self-heal, producing the spectral signature of the π-stacked ordered film in the absorption spectrum. All measurements described in later sections were made at room temperature with such ordered films.

It is also possible to prepare thinner uniform films of **1** by vacuum evaporative deposition onto a metal or ITO support. Although this technique has proved more difficult to specifically control the thickness of the film, viable films useful for device applications can be prepared. This mode of film preparation also wastes material, with the entire surface of the vacuum evaporator becoming similarly coated in the process: as a result, the evaporation method is not recommended for preliminary structure-performance studies, but rather only for optimization for specific applications with a chosen material.

Mechanism of Charge Separation in a Solid Thin Film of 1

Unexpectedly, the completely symmetric, unbiased, undoped sandwich cell prepared as described in the previous section (ITO-1-ITO) produces, upon visible excitation, a significant and stable open-circuit photovoltage and short-circuit photocurrent.[17,18] With the filtered (λ > 400 nm) illumination of a 150-W xenon lamp (intensity about 150 mW/cm²), a stable photocurrent of about 0.4 mA/cm² is produced, with the illuminated ITO face charging negative, i.e., acting as a photoanode. After a small (<10%) initial decay, photocurrent production is sustained without noticeable
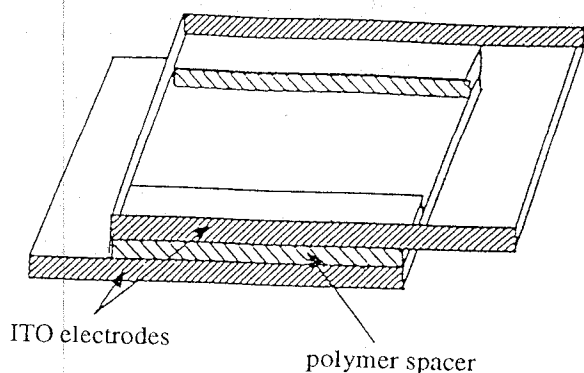

ITO electrodes

polymer spacer

Fig. 4. Schematic View of a Liquid Crystalline Thin Layer Sandwich Device.[17]

decay for months of repeated exposure to light. That the observed effect is initiated by photoexcitation is clear from the directional charge reversal attained by switching the face of illumination of the sandwich cell. The observed photocurrent is linearly dependent on the incident light intensity at values below a light flux of 10^{15} photons s⁻¹ cm⁻¹. The photoaction spectrum (a plot of the relative intensity of photocurrent on incident wavelength) is dependent on the thickness of the absorbing layer: with thicknesses at or below about 1 μm, a close parallel between the action spectrum and the diffuse reflectance absorption spectrum of the film is observed. With thicker films, the relative intensity of photocurrent produced by wavelengths greater than 500 nm increases so that in a cell of about 3 μm thickness nearly equal photocurrent production is observed upon excitation into the Soret and Q bands, despite the much larger extinction coefficient of the former.

The observation of photovoltage and photocurrent across an unbiased, absorptive, ordered organic layer requires the production and spatial separation of opposite charge carriers in the photoexcitation event. Efficient photoinduced charge separation in this sandwich cells requires two separate photodriven events: (1) preferential injection of one of the charge carriers (an electron or a hole) at the illuminated electrode; and (2) a substantial difference in the photoconductivity and dark conductivity of the bulk absorptive layer.

The observation that the illuminated electrode charges negative implies preferential electron injection at the excited porphyrin-ITO interface, a phenomenon that can be rationalized as resulting from the greater orbital overlap of the photoproduced exciton with the empty conduction band levels of ITO.[17] This result is full accord with the results of Hall and coworkers who observed similar charging effects in their measurements of open-circuit photovoltages obtained with different metal electrodes employed in phthalocyanine solar cells that were prepared and studied under vacuum.[19] It is also compatible with currently accepted mechanisms for photovoltage production (although much less efficient than in the cells discussed here) across single crystals of organic compounds, usually zone-refined polycyclic aromatics.[20-22] In such materials, exciton migration to the surface of the contacting semiconductor electrode, followed by dissociation and injection of one carrier, is the dominant mode for photocurrent production.[20,23-27] Thus, we suggest that, with no applied bias, the preferential photoinjection of electrons into the illuminated electrode is responsible for the photoinduced asymmetry in these sandwich cells.[17] The injection process itself thus resembles spectral sensitization of a semiconductor electrode.[28]

Both the unusual magnitude of the observed photocurrent and the observed dependence of the photoaction spectra on cell thickness also require a second mechanistic photoprocess: the bulk generation of charge carriers and a means by which these carriers can efficiently migrate to the interface between the conductive ITO interfaces. For appreciable changes in dark and light-induced conductivity, the photoresistance of the cell must decrease with increasing numbers of such charge carriers and must depend on their spatial distribution within the bulk layer.[17] Both requirements are met in the ITO-porphyrin-ITO sandwich cell described above.

These two effects can be represented in the equivalent circuit model illustrated in Fig. 5.[17] In this model, carrier injection is represented as a variable current source j_f operating in parallel with a capacitance C and a shunt resistance R_s. The bulk resistance R is decreased during irradiation as more charge carriers are produced in the bulk, with the number of carriers (and, hence, the change in resistance) being sensitive to the incident light intensity and the interfacial voltage. For thicker layers, incomplete light penetration adversely affects the through-layer conductivity and accounts for the dependence of the photoaction spectra on film thickness.

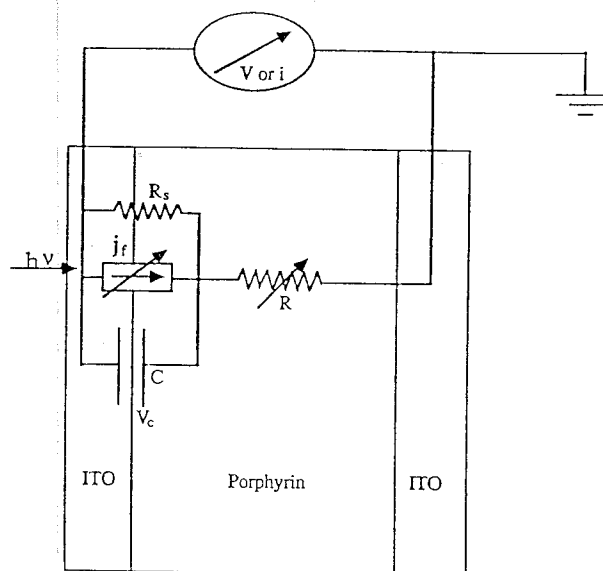These mechanisms are also reasonable extrapolations

Fig. 5. An equivalent circuit model for the operation of an illuminated ITO-π-stacked porpyrin-ITO sandwich cell.[17] A variable current source j_f is in parallel with a capacitance C and a shunt resistance R_s, with photocurrent flowing as changes in the bulk resistance R are induced by photoexcitation of the light-absorbing layer.

to the solid state from solution phase photophysical behavior described for other columnar discotic compounds. For example, the magnitude of exciton coupling in face-to-face porphyrin dimers and trimers has been shown to depend on solvation and local order,[29] with a low-lying virtual charge transfer state near the lowest singlet being invoked to explain the increase in the internal conversion rate constant at the expense of other radiative and radiationless processes and to account for the invariance of the aggregate lifetimes (dimer and trimer) compared with that of the monomer. Charge transfer complex formation in solution is also favored by the presence of interacting molecular aggregates, with polarized absorption spectra of oriented thin films indicating that charge transfer takes place along the stacked array.[30] Markovitsi and coworkers have also demonstrated that one-dimensional singlet[31] and triplet[32] energy migration can take place along the stacked axes of columnar liquid crystals. These studies permit the determination of a singlet exciton hopping time of 32 fs, a singlet exciton diffusion coefficient of 2.0×10^{-2} cm^2 s^{-1}, and an intrinsic trap molar fraction of 10^{-3} in stacked triphenylenes.[31] Although somewhat slower hopping times (0.4 - 68 ps) were reported in the triplet states of stacked phthalocyanines,[32] more efficient energy migration was again observed in the liquid crystalline than in the solid, crystalline phase of the same compound.

Phase-dependent Time-Resolved Microwave Conductivity of 1

Consistent with the requirement for substantially altered bulk conductivity for porphyrin 1 films, both 1a and 1b exhibit very low intrinsic dark conductivity.[33] Upon production of a small concentration (less than 10 μM) of electron-hole pairs by a short pulse (2 - 20 ns) of ionizing radiation (3 MeV electrons from a Van de Graaff accelerator), however, changes in conductivity resulting from the presence of mobile charge carriers can be measured by a contactless time-resolved microwave conductivity technique. The observed conductivity decays on a time scale much longer than the pulse-width, with substantially enhanced decay rates being observed at temperatures above the transition temperatures into and out of the discotic liquid crystalline phase.[33] The observation that long-range columnar order is essential for the conductivity was interpreted as evidence for the general supposition that electrons and/or holes move rapidly along the axis of the column-stacked π-systems, as had been asserted earlier for ordered phthalocyanines.[24,34] The minimum value for carrier mobility in the solid phase of 1a and 1b indicates small polaron motion between interacting groups, with a jump time of 0.6 ps being estimated for

the excited state of **1b** at room temperature. Clearly, given that charge transport can occur very rapidly within a self-assembled array of porphyrin moieties, such aggregates constitute reasonable synthetic model systems to crudely mimic energy and charge transport in biologically important light collection arrays.[35]

Charge Trapping in Thin Films of 1b

These same films can be used as the basis for a high density, high speed, low volatility, reusable material for data storage.[1,36,37] The large difference between bulk conductivity in the dark and under illumination permits dark charge trapping which, in turn, can be read as a stored electro-optical data point as either a dark open-circuit voltage or a light-induced short-circuit discharge photocurrent. This information can be written, read, and/or erased by simultaneous application of an electric field and a light pulse.

By applying a constant bias during pulsed irradiation or a pulsed bias under steady illumination, charge trapping takes place across of thin film of **1b** in which initially vacant traps within the ordered layer are filled with electrons. The high dark resistivity of this layer ($>10^{14}$ Ω·cm) makes it possible to freeze these charge carriers by switching off the light. The written information can then be read out later by irradiation with a "read beam", producing a release of electrons by an anodic discharge spike for information stored under a negative bias.[37] Holes can be trapped and released analogously with an initial positive bias.[37]

Time-resolved photophysical studies have shown that the rise-time associated with the write pulse with **1b** is in the nanosecond range.[1,37] Storage densities of about 3Gb/cm^2 have been estimated from determination of spatial resolution by the use of the highly localized electric filed supplied by the sharp tip of a scanning tunneling microscope.[36,37] The stored information can be accessed many times, the short-circuit current readout signal retaining more than 60% of its initial readout value after 1500 readings, even better results being probable after employing a refreshing cycle.[36,37] No irreversible changes in the film composition could be detected after even one billion charge-discharge cycles.[36,37]

CONCLUSIONS

The synthesis of a family of columnar discotic liquid crystalline porphyrins has provided access to an interesting class of materials that exhibit unusual photovoltaic effects and can be employed in a new kind of opto-electronic information storage device. The compounds's "self-healing"

through π-stacking in the liquid crystalline phase makes practical the fabrication of ordered solid films of this family. The contrasting dark resistivity and high photoconductivity of these arrays is a critical criterion for successful charge separation and trapping.

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