# Halide effect in electron rich and deficient discotic phthalocyanines †‡§

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A series of discotic octa- and tetra-alkylthio substituted phthalocyanines containing four Cl, Br, I atoms or twelve fluorine atoms have been prepared. All compounds display columnar mesomorphism as confirmed by polarized optical microscopy, thermal analysis, and variable temperature X-ray diffraction. Phthalocyanines containing halide atoms do not crystallize but form glassy or partially crystalline hexagonal columnar phases. Glass transition temperatures increase with increasing size of the halide atoms and with decreasing length of the alkyl chains. In contrast, all octa- and tetra-alkylthio substituted phthalocyanines crystallize and octa-substituted derivatives with aliphatic chain lengths of  $C_{5-7}$  exhibit tilted (rectangular) columnar mesophases. Cyclic and differential pulse voltammetry, UV-Vis spectroscopy, and quantum chemical calculations at the DFT level have been employed to determine frontier orbital energies of all synthesized and some reference phthalocyanines. Octa- and tetra-alkylthio substituted phthalocyanines are typical p-type semiconductors and the introduction of four Cl, Br, or I atoms lowers frontier orbital energies by only up to 0.1 eV and the optical gap by up to 0.03 eV. A significant decrease in LUMO energy by 0.5 eV to about -4 eV is observed for the fluorinated phthalocyanine, which is a value right at the border of organic n-type semiconductors that may be stable in air.

# Introduction

Discotic liquid crystals (DLCs) have been investigated as an alternative class of organic semiconductors.<sup>1</sup> These compounds may self-organize into columnar stacks that provide high and anisotropic charge carrier mobilities along the columnar stacks due to overlapping  $\pi$ -orbital systems.<sup>2,3</sup> In addition to efficient charge transport and the advantages generic to most organic semiconductors, such as low temperature solution processing and synthetically adjustable properties, DLCs promise to be capable of self-healing and can be used in the formation of highly anisotropic materials.

Phthalocyanines (Pcs) have been used as semi- and photoconductors for decades because of their exceptional electrooptical properties and high stability.<sup>4,5</sup> Their large discoid conjugated macrocycle and strong  $\pi$ - $\pi$  stacking forces make them ideal building blocks for DLCs.<sup>6-9</sup> High "intrinsic" charge carrier mobilities of 0.2–0.4 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> measured by time resolved microwave conductivity have been reported for conventional columnar mesophases of discotic Pcs.<sup>10</sup>

While charge carrier mobility benefits from the high  $\pi$ – $\pi$  stacking forces of Pcs<sup>11</sup> these forces are also responsible for the formation of highly viscous thermotropic columnar mesophases and strong aggregation in solution. Both properties complicate processing of columnar mesophases of discotic Pcs into aligned monodomains that are essential for device applications. More fluid columnar mesophases of discotic Pcs are usually more amenable to alignment and techniques such as zone casting,<sup>12</sup> surface and confinement directed alignment,<sup>9,13,14</sup> and mechanical alignment *via* intermediate lyotropic mesophases<sup>15</sup> have been successfully applied.

Crystallization of DLCs is another obstacle for device applications if major structural rearrangements and polycrystalline materials of small domain size are generated, as it is the case for most discotic Pcs. The "macroscopic" charge conduction of polycrystalline films is drastically diminished because charge carriers are trapped at grain boundaries between crystalline domains, although values of "intrinsic" mobility are usually higher in the crystalline phases than in mesophases since  $\pi$ - $\pi$ interactions are less disturbed by molecular motion.<sup>10,16,17</sup> An obvious remedy is the suppression of crystallization by the formation of anisotropic glasses of hexagonal columnar (Col<sub>h</sub>) mesophases or discotic plastic crystal phases that may also improve mechanical properties and charge conduction.<sup>17,18</sup>

General approaches to glassy DLCs have been developed but mostly for triphenylenes. The exchange of one ether linkage in hexaalkoxy triphenylenes by an ester group suppresses crystallization and has been studied in great detail.<sup>19,20</sup> Linking DLCs together to main-chain oligomers also ensures the formation of

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glasses but these materials could not be processed into larger domains of uniform alignment<sup>21</sup> with the possible exception of star-shaped oligomers.<sup>22</sup> However, stable glasses are already formed by dimers of differently substituted triphenylenes and their columnar mesophases can be uniformly aligned.<sup>23</sup> The examples of discotic Pcs forming anisotropic glasses upon cooling of the preceding columnar mesophases are limited to derivatives substituted with dendrons<sup>24</sup> and mixtures of unsymmetrically substituted discotic Pcs.<sup>25</sup>

Applications of discotic Pcs in electronic devices not only require optimization of their phase behaviour and alignment but also their electronic properties such as their frontier orbital energies. Adjustment of frontier orbital energies permits control over charge injection at electrode interfaces or between different organic semiconductors.

Electronic properties of Pcs have been studied in great detail<sup>26-28</sup> but few studies, other than on charge conduction, have been conducted on discotic or potentially discotic Pcs.<sup>14,29-32</sup> Pcs are inherently electron rich p-type semiconductors and this especially applies to discotic Pcs because most of them are substituted with  $\pi$ -donating alkyl, alkyloxy, and alkylthio groups. Electron deficient Pcs are sparse and have been prepared by exchanging the benzene rings with *N*-heterocycles,<sup>28,32,33</sup> by perfluorination of the macrocycle and attached alkyl groups,<sup>28,34</sup> and by the attachment of  $\pi$ -electron withdrawing sulfonate groups.<sup>35</sup> We are aware



Scheme 1 Reaction conditions: (a) 1.5 eq. RSH, Cs<sub>2</sub>CO<sub>3</sub>, dimethylimidazolidinone (DMI) or DMF, 50 °C (**2–5**) or -10 °C (**1**); (b) 2.5 eq. RSH, Cs<sub>2</sub>CO<sub>3</sub>, DMI, 50 °C; (c) 1.4 eq. Li, pentanol, rfl., 2h, Ar followed by 8 eq. CuAc<sub>2</sub>, HAc, 60 °C, 1 h for **18–27** or quinoline/1 eq. CuCl<sub>2</sub>/180 °C for **17**.

of only three types of electron deficient discotic Pcs, two are octa-substituted with  $\pi$ -electron withdrawing carbonyloxy and sulfonyl groups,<sup>29,31</sup> and one is based on the tetrapyr-azinoporphyrazine core.<sup>32</sup>

Presented here are the synthesis, mesomorphism and determination of frontier orbital energies of discotic copper(II) phthalocyanines (Pcs) **17–27** (Scheme 1) as an extension of our previous work on alkylthio- and chorine-substituted Pcs.<sup>25,36</sup> Introduction of halide atoms resulted in the formation of glassy hexagonal columnar mesophases (Col<sub>h</sub>) and tetra-alkyl substitution suppressed the formation of titled columnar mesophases. Fluorinated Pc **17** has sufficiently low lying frontier orbitals to function as an n-type discotic material.

## **Results and discussion**

## Synthesis

Pcs 17-27 were synthesized according to Scheme 1. Starting materials 1, 2, and 5 are commercially available; phthalodinitriles 3 and 4 were prepared following literature procedures.<sup>37</sup> Phthalodinitriles 7-14 were obtained from 2-5 by nucleophilic substitutions with alkylthiols at 50 °C in the presence of Cs<sub>2</sub>CO<sub>3</sub>. About 10% higher yields were obtained with dimethylimidazolidinone as solvent when compared to DMF under the same conditions. Mono-substituted phthalodinitriles 7-9 and 11 were obtained as mixtures with di-substituted phthalodinitriles and were separated by fractionated crystallization and column chromatography. All other mono-and di-substituted phthalodinitriles 10 and 12-16 did not contain mixtures of side products and were purified by column chromatography. Subsequent cyclization of 7-16 using the established lithium pentanolate procedure<sup>38,39</sup> gave the corresponding Pcs 18-27 in fair yields of 50-60%. Pcs 24-27 were also prepared in the presence of a large excess of lithium octanolate at 80-90 °C, which increased the yield by up to 10% in comparison to the lithium pentanolate procedure but require a reaction time of 3 d instead of 2 h. Compounds 7, 10, 14, 16, 18, 21, 25 and 27 have been previously synthesized.25,40-43

Altered conditions were required for the preparation of Pc 17; 1 was substituted at -10 °C to ensure the regioselective substitution at the 4 and 5 positions to give a mixture of monosubstituted phthalodinitrile 6 and di-substituted phthalodinitrile that was separated by column chromatography. The 1,2,4substitution pattern of 6 was confirmed by <sup>19</sup>F and <sup>13</sup>C NMR spectroscopy. Cyclization of 6 in lithium pentanolate produced a mixture of Pcs containing octylthio and pentyloxy groups suggesting that fluorine atoms were substituted by pentanolate groups under these conditions. The amenability of fluorine atoms of perfluoro Pcs to nucleophilic substitution has been demonstrated previously.<sup>44</sup> Pc 17 was prepared from 6 in a mixture of quinoline and anhydrous CuCl<sub>2</sub> at 180 °C in 24% yield.

All Pcs were characterized by UV-Vis and IR spectroscopy as well as by MALDI-MS and elemental analysis. The results agreed with the theoretically expected values and in the case of Pcs 18,<sup>25</sup> 21,<sup>40</sup> 25<sup>42</sup> and 27<sup>25,41</sup> also with reported values. It is assumed that Pcs 17–23 were formed as statistical mixtures of four regioisomers but all attempts to verify this by NMR measurements on metal-free precursors were not successful due

to strong aggregation even in solvents such as pyridine and interfering solvent peaks in the aromatic range. Equally unsuccessful were attempts to separate the isomers of Pc **18** by HPLC on silica and mixtures of toluene and pyridine as solvent. Some less aggregating tetra-substituted Pcs have been studied in more detail and, with few specific exceptions,<sup>45</sup> occurred as statistical mixtures of regioisomers (12.5%  $C_{4h}$ -, 25%  $C_{2v}$ -, 50%  $C_s$ -, and 12.5%  $D_{2h}$ -isomer).<sup>39,46</sup>

#### Mesomorphism

All eleven Pcs **17–27** display thermotropic columnar mesomorphism as well as lyotropic mesomorphism in organic solvents. Their thermotropic mesomorphism was studied by polarized optical microscopy (POM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and variable temperature X-ray diffraction (XRD) and is summarized in Fig. 1. Their lyotropic mesomorphism is not presented here but has previously been reported for Pcs **18** and **27** as well as related compounds.<sup>25,36</sup>

Variable temperature POM measurements revealed no changes to the birefringent textures upon heating from 20 °C to temperatures above 300 °C with the exception of melting transitions for Pcs 17, 24, 26 and 27. Optically visible decomposition sets in at about 320 °C for all Pcs but Pc 17 that already decomposes at about 250 °C. Consequently, no natural defect textures could be obtained but areas with fan-shaped textures were observed for all eleven Pcs and are characteristic of columnar discotic mesophases. Pcs 18, 19, and 20 show a sudden

17	Col. cryst	49.2 (-9.44)	Col <sub>-</sub> -	>200
	oon oryst	40.9 (8.27)	001	2 docompt
10		-8.5 (T <sub>g</sub> )	Col	>260 > docomo
10	COI <sub>h</sub> glass	-11.0 (T <sub>g</sub> )	COIh -	- decomp.
	0.1.1.1	9.6 (T <sub>g</sub> )	0.1	>260
19	Col <sub>h</sub> glass	8.1 (T <sub>g</sub> )	COI <sub>h</sub> -	→ decomp.
		35.7 (T <sub>g</sub> )	_	>250
20 21 22	Col <sub>h</sub> glass Cryst Col <sub>h</sub> glass	32.9 (T <sub>q</sub> )	Col <sub>h</sub> - Col <sub>h</sub> - Col <sub>h</sub> -	→ decomp.
		3.4 (-12.10)		>250 .
		-8.2 (12.05)		decomp.
		43.1 (T <sub>g</sub> )		>260
		40.1 (T <sub>q</sub> )		decomp.
23	Cryst	-23.4 (-0.74)	Col <sub>h</sub> -	>260
		-24.0 (0.91)		→ decomp.
		109.8 (-18.81)		>260
24	Cryst	69.6 (2.66)	Col <sub>rd</sub> -	→ decomp.
		9.5 (-7.75), 17.4 (-2.05)		>260
25	Cryst	0.1 (12.35)	Col <sub>rd</sub> -	→ decomp.
26	Cryst	80.8 (-32.52)	Col <sub>rd</sub> -	>260
		19.1 (21.91)		decomp.
27	Cryst	-12.2 (-11.37)	Col <sub>h</sub> -	>260
		-24.1 (14.70)		→ decomp.

Fig. 1 Phase behaviour of Pcs 17–27. Listed are onset temperatures in °C ( $\Delta$ H in kJ mol<sup>-1</sup>) and mid-points of glass transitions measured by DSC at 5 °C min<sup>-1</sup>and 10 °C min<sup>-1</sup>, respectively. Approximate decomposition temperatures are given as onset of weight loss (-0.2 wt%) measured by TGA at 2 °C min<sup>-1</sup>.

decrease in viscosity at 80-100 °C upon heating but these events do not coincide with their glass transitions determined by DSC, which occur at much lower temperatures. What is observed by DSC are slopes in the baseline between 60 and 130 °C that may be caused by weak and broad 2nd-order transitions.

Decomposition temperatures were independently determined by TGA in He at a heating rate of 2 °C min<sup>-1</sup>. The first main weight loss occurs at temperatures between 290 °C and 310 °C for Pcs **18–27** but the onset of weight loss, defined as loss of 0.2 wt%, is at much lower temperatures of 250 °C to 260 °C. Cleavage of the S–alkyl bond is proposed as the first thermal decomposition step because typical fragment ions of aliphatic chains and no halides were observed by simultaneous EI-MS analysis of the evolved gases. Cleavage of the S–alkyl bond is also the primary fragmentation in CI-MS.<sup>25</sup> The onset of weight loss of Pc **17** is at 200 °C, which suggests that the S–alkyl bond is easily cleaved in **17** presumably because of the electron withdrawing fluorine atoms.

DSC measurements revealed glass transitions for Pcs **18–20** and **22** while Pcs **17**, **21**, and **23–27** showed melting transitions (Fig. 1 and 2). The melting transitions of **17**, **21** and **23** are broad and crystallization is suppressed at cooling rates of  $5 \,^{\circ}$ C min<sup>-1</sup> or faster but proceeds for **17** within several hours at 25  $^{\circ}$ C. Broad humps and slopes in the baselines of the DSC curves of Pcs **18–22** suggest additional thermal transitions between 60  $^{\circ}$ C and 130  $^{\circ}$ C that coincide with a decrease in viscosity observed by POM. However, no coinciding changes are observed in the variable temperature XRD patterns other than the typical small shifts in d-spacings with temperature.

Unusually strong is the odd–even effect observed for the reversible melting temperatures of Pcs 24–27. Pcs 24 and 26 with odd numbered hydrocarbon chains melt at almost 100 °C higher temperatures than their even numbered counterparts. We note that Pc 27 melts at a much higher temperature of 74 °C (onset) in its first heating run and that Pcs 24–26 show several weak crystal–crystal transitions that indicate rich crystalline polymorphism. Interestingly, no systematic odd–even effect was detected in metal-free and copper(II) octa-alkoxy substituted Pcs.<sup>10,47</sup>

Phase assignments given in Fig. 1 are based on variable temperature XRD analysis. Isomer mixtures of Pcs 17-23



**Fig. 2** DSC curves of Pcs **17–21** on heating at 10 °C min<sup>-1</sup> ( $T_g$  = glass transition;  $T_m$  = melting transition). The curves were shifted for clarity.

 Table 1
 Mesophases and parameters determined by XRD. Tables of all reflections are provided in the ESI

Compound	<i>T</i> /°C	Phase	Lattice parameters/Å	Intracolumnar stacking/Å
17	25	Colherve	a = 25.4	3.30
	90	Colh	a = 26.4	3.31
18	25	Colh	a = 24.4	3.35
19	25	Col <sub>h</sub>	a = 22.1	3.37
20	25	Col <sub>h.glass</sub>	a = 25.4	3.41
21	25	Colh	a = 25.9	3.36
22	25	Col <sub>h.glass</sub>	a = 20.4	3.34
	100	Colh	a = 20.8	3.35
23	25	Colh	a = 20.8	3.35
24	130	Col <sub>r</sub>	a = 43.4, b = 21.6	3.5
25	25	Col <sub>r</sub>	a = 45.48, b = 23.28	3.5
26	100	Col <sub>r</sub>	a = 47.7, b = 25.5	3.6
27	25	Col <sub>h</sub>	a = 27.3	3.5



Fig. 3 1D-XRD diffraction patterns of Pcs 17–21 and 26 at 25 °C. The patterns were shifted for clarity.

containing four alkylthio groups all display hexagonal columnar mesophases (Table 1 and Fig. 3). Diffraction patterns of Pcs 17, 21 and 23 contained the (11) and (20) reflections in addition to the intense fundamental (10) reflection, which unambiguously identifies a 2D hexagonal symmetry of the columnar packing. Pcs 18–21 only show the (10) reflection and their hexagonal packing was verified by 2D XRD measurements along the columnar axis of shear aligned films that revealed the characteristic hexagonal pattern (Fig. 4b).<sup>48</sup>



**Fig. 4** (a) 2D XRD pattern of Pc **20** orthogonal to the aligned columnar stacks; arrow marks the broad reflection at about  $2\theta = 12^{\circ}$ . (b) 2D XRD pattern of Pc **18** along the (partially) aligned columnar stacks.

Other common reflections observed in the diffraction patterns of Pcs 17–27 are a broad halo at  $2\theta = 19-24^{\circ}$ , indicative of an amorphous packing of aliphatic side chains, and a reflection of the intracolumnar  $\pi$ - $\pi$  stacking at  $2\theta = 25-27^{\circ}$ . The reflection of the intracolumnar  $\pi$ - $\pi$  stacking is intense for tetra-alkylthio substituted Pcs 17–23 but weak and broad for octa-alkylthio substituted Pcs 24–27, which implies that Pcs 17–23 have a much higher intracolumnar stacking order than Pcs 24–27. Tetraalkylthio substituted Pcs also show shorter stacking distances by up to 0.3 Å than octa-alkylthio substituted Pcs.

The halo of the aliphatic side chains is unusually narrow for Pc **17** at temperatures below its broad melting transition. This narrowing suggests that partial crystallization of the side chains occurs and verifies that the phase transition detected by DSC is indeed that of partially melting/crystallizing side chains. Consequently, the low temperature Col<sub>h</sub> phase of Pc **17** is labelled Col<sub>h,cryst</sub> in contrast to the fully crystalline tilted columnar phases of Pcs **21** and **24–27**. The restricted crystallization of the side chains in Pc **17** is likely the reason why **17** does not adopt a tilted columnar phase typical for most crystalline phases of discotic Pcs.<sup>8,6,49</sup>

Diffraction patterns of Pcs 18–20 and 22 contain an additional broad reflection (halo) at about  $2\theta = 12^{\circ}$  that increases in intensity with increasing size of the attached halide atoms and is absent in Pcs 21 and 23. 2D XRD of an aligned sample of Pc 20 reveals that this reflection aligns with the lattice of the 2D hexagonal columnar phase (Fig. 4a). Consequently, this reflection likely originates from a periodic lateral (intercolumnar) packing of halide atoms. This periodic packing must be exclusively intermolecular in nature because the spacing of 7–8 Å does not match any distances between halide atoms within one molecule of Pcs 18–20 and 22.

Both intercolumnar and intracolumnar packing distances are affected by the different halide atoms in Pcs **17–20** as indicated by the shifting maxima of the (10) and (001) reflections in Fig. 3. Unexpectedly, the lattice constant "*a*" decreases from 26 Å to 24 Å to 22 Å when the size of the halide atoms was increased from F to Cl to Br, respectively, and then increased again to 25 Å and 26 Å for substituents I and H in Pcs **20** and **21**, respectively.

The intracolumnar stacking distance slightly increases with increasing size of halide atoms from 3.30 Å in **17** to 3.41 Å in **20** and is 3.36 Å in **21**. The increase in stacking distance of 0.1 Å between Pcs **17** and **20** is much smaller than the difference in van der Waals radii between F and I of 0.51 Å.<sup>50</sup> This discrepancy is likely a result of differences in average mutual rotation angle between stacked Pc cores although contributions of electronic differences in average mutual rotation as be the reason for the unexpected changes in intercolumnar spacing whereas the observed small differences in stacking distance should only have a marginal effect on the intercolumnar spacing.

Diffraction patterns of octa-alkylthio substituted Pcs 24–27 confirm the formation of conventional crystal phases as well as rectangular columnar mesophases for Pcs 24–26<sup>51</sup> and a hexagonal columnar mesophase for Pc 27. The Patterson symmetry of the Col<sub>rd</sub> phases of 25 and 26 is likely *c2mm*, all observed reflections obey h + k = 2n, while the symmetry of 24 is *p2gg* because of the presence of a (43) reflection  $(h + k \neq 2n)$ . Octa-alkylthio Pcs with longer alkyl chains than octyl have been

reported to all form hexagonal columnar mesophases.<sup>52</sup> A change from Col<sub>h</sub> to Col<sub>rd</sub> mesophases with decreasing length of aliphatic chains is common in discotic Pcs<sup>5,8,53,54</sup> and other discotic liquid crystals.55 The high propensity of CuPc to form tilted columnar stacks may be reasoned with the formation of axial Cu-N interactions between adjacent macrocycles.49

In contrast, shortening of octyl to pentyl chains in tetraalkylthio substituted Pcs 22 and 23 does not induce a tilted columnar mesophase. A change from octa- to tetra-alkylthio substitution and likely the presence of a mixture of four isomers are responsible for the suppression of the formation of tilted columnar mesophases, but the presence of halide atoms is not required. Suppression of crystallization in Pcs 18-20, on the other hand, is specific to the presence of halide atoms because Pcs 21 and 23, that do not contain halide atoms but also are mixtures of four isomers, do crystallize.

Glass formation in DLCs is associated with restricted rotation of the discotic molecules about their stacking axis<sup>19,56</sup> and this model is used here for reasoning the observed "halide-effect". The activation energy for rotation about the stacking axis should increase with increasing size (van der Waals radius) of the halide atoms and rotational barriers in Pcs 18-20 are apparently sufficiently high to freeze in molecular motion before crystallization occurs. The observed short stacking distances and the increase in glass transition temperatures with increasing size of halide atoms are consistent with this model.

Specific halide-halide interactions may also add to the rotational barrier and have been used in crystal engineering.57 However, present models propose 90° and 180° angles between two interacting halide-C groups as ideal geometry,58 which excludes intracolumnar and suggests intercolumnar halidehalide interactions as contributors to the rotational barrier. In fact, the broad reflection at about 7-8 Å observed in the XRD patterns of Pcs 18-20 may be a result of periodic packing due to intercolumnar halide-halide interactions. A conclusive analysis, however, requires more detailed experimental and theoretical studies that are beyond the scope of this work.

Other examples of "halide effects" in DLCs include the promotion of mesomorphism in discotic triphenylene derivatives. Tribromo-trialkoxy triphenylene displays a hexagonal columnar mesophase whereas the non-brominated trialkoxy triphenvlene is not mesomorphic.<sup>59</sup> However, no glass transitions but crystallizations have been reported for the more fluid and less tightly stacked columnar mesophases of tribromo-trialkoxy and tribromo-trialkylthio triphenylenes.35

#### **Electronic properties**

Pcs 17-21, 26 and reference compound perfluoro phthalocyaninato copper (28 in Fig. 5) were studied by cyclic voltammetry (CV), UV-Vis spectroscopy and quantum chemical calculations at the DFT level of theory to determine their frontier orbital energies and the contributions of the macrocycles to the frontier orbitals. All Pcs were measured in CH<sub>2</sub>Cl<sub>2</sub> solution at concentrations of 2–6  $\times$   $10^{-5}$  M and compounds 19 and 26 were also run in pyridine to test for aggregation effects. Tetrabutylammonium perchlorate (TBAP) at a concentration of 0.1 M was added as the supportive electrolyte in all measurements.

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1.2x10<sup>-6</sup>

Fig. 5 Cyclic voltammograms of Pcs 17 (solid line), 18 (dashed line) and 21 (dash doted line) in 0.1 M TBAP-CH<sub>2</sub>Cl<sub>2</sub> solution vs. Ag/Ag<sup>+</sup>.

Table 2 Half-wave potentials ( $E_{1/2}$ , V vs. Ag/AgCl) of Pcs determined by cyclic voltammetry in CH2Cl2 solution (2-6 × 10-5 M, 0.1 M TBAP, glassy carbon working electrode, scan rate of 0.100 V s<sup>-1</sup>)

CuPc	$E_{1/2} (OX)^a/V$ vs. Ag/Ag <sup>+</sup>	$E_{1/2}$ (Red-I) <sup><i>a</i></sup> /V <i>vs.</i> Ag/Ag <sup>+</sup>	$E_{1/2}$ (Red-II) <sup><i>a</i></sup> /V <i>vs.</i> Ag/Ag <sup>+</sup>	$\frac{\Delta E_{\rm gap}{}^{b}/\rm V}{(=\rm eV)}$
17	1.47	0.38	0.65	1.85
18	1.06	-0.33 -0.80	-1.08	1.85
19	1.01	-0.88	-1.01	1.89
19 <sup>c</sup>		-0.76	-0.97	
20	0.97	-0.87	-1.19	1.84
21	0.85	-0.99	-1.27	1.84
26	0.94	-0.91	-1.15	1.85
<b>26</b> <sup>c</sup>		-0.79	-1.09	
28	1.85	n.o. <sup>d</sup>	n.o. <sup>d</sup>	_

<sup>*a*</sup>  $E_{1/2} = (E_{p,a} + E_{p,c})/2$  at 100 mV s<sup>-1</sup>. <sup>*b*</sup> Δ $E = E_{1/2}$  (first oxidation) –  $E_{1/2}$  (first reduction) = HOMO–LUMO gap. <sup>*c*</sup> Measurement in pyridine under otherwise identical conditions. The oxidation potentials of 18 and 24 are outside the electrochemical window of pyridine. d The first two reduction peaks could not be resolved with certainty presumably due to strong aggregation. A peak was observed at -0.84 V by differential pulse voltammetry and likely is the third reduction step.

Pcs 17-21 and 26 in CH<sub>2</sub>Cl<sub>2</sub> solution show one quasi-reversible oxidation and two quasi-reversible one-electron reductions in the covered electrochemical window of -2.0 V to 2.0 V (Table 2 and Fig. 5). Pc 28 was quasi-reversibly oxidized but the 1st and 2nd reduction peaks are too weak and broad to be determined with certainty presumably because of low solubility and strong aggregation. A value of -0.1 V (vs. Ag/AgCl) was reported in the literature for the 1st reduction potential but no experimental details were given.60

The quasi-reversible character of the redox processes was confirmed by a constant increase of  $\Delta E_{\rm p}$  with increasing scan rates and a  $\Delta E_{\rm p}$  larger than 0.059 V (approximately 0.100 V) at a scan rate of 0.100 V s<sup>-1.61</sup> The peak currents increased linearly as a function of the square root of scan rates  $(I_p/\nu^{1/2})$  for scan rates ranging from 0.050-0.500 V s<sup>-1</sup>, indicating that the electrode reactions are merely diffusion-controlled for all redox processes. A diffusion-controlled mass transfer mechanism is also supported by the fact that peak current ratios  $(I_{pc}/I_{pa})$  for all processes are approximately unity and do not vary considerably with scan rates.

Pcs 18–20 and 26 have similar redox potentials while 21 is easily oxidized and more difficult to reduce by about 0.1 V. Pc 17 is significantly more electron deficient, manifested by a +0.5 V shift of the oxidation and reduction potentials in comparison to 26. In contrast, the energy gap between oxidation and reduction potentials is practically constant for all measured compounds with values between 1.84 V and 1.89 V.

Frontier orbital energies of the air stable n-type semiconductor Pc **28** were determined by CV and optical gap measurements in solution and are in good agreement with values obtained by other techniques.<sup>62,63</sup> The oxidation potential of discotic Pc **17** is shifted by -0.38 V in comparison to Pc **28**, which makes Pc **17** a borderline case n-type semiconductor with regard to air stability.<sup>60,64</sup>

A comparison of the reduction potential of Pc 17 (-0.34 V vs. SCE = Ag/AgCl + 0.045) with reported 1st reduction potentials of electron deficient octa-carbonyloxy and octa-alkylsulfonyl substituted discotic Pcs<sup>31</sup> and octa(dodecyl)tetrapyr-azinoporphyrazines<sup>32</sup> (-0.45 V, -0.14 V and -0.41 to -0.55 V vs. SCE, respectively) places Pc 17 second of the four. However, replacement of the thioether groups of Pc 17 by  $\pi$ -electron withdrawing groups (*e.g.* by oxidation of the thioether to alkyl-sulfonyl groups) should generate a derivative that is more electron deficient than Pc 28.

Exchange of four SR groups by I, Br, and Cl (*e.g.* conversion of Pc 27 to Pcs 18–20) exerts only minor changes on the redox potentials despite the differences in electronegativity between S, I, Br, and Cl. A small systematic change is observed for their oxidation potentials that increase from 0.85 V to 1.06 V in the order 21 < 26 < 20 < 19 < 18. The large shifts in redox potentials observed for the fluorinated Pcs 17 and 28 are mainly generated by the additional F-atoms in 1,4-positions. Comparative DFT calculations on Pc 31 (Fig. 6), the fluorinated analogue of Pc 18, predict no significant difference in frontier orbital energies between the two.

Optical HOMO–LUMO gaps were measured by UV-Vis spectroscopy in pyridine solution. A small but systematic increase of the gap from 1.67 eV to 1.77 eV in the order 26 < 17 < 18 < 19 < 20 < 21 < 28 was determined. Pyridine was used because solutions that are optically free of aggregates can be obtained at concentrations between  $10^{-5}$  M and  $10^{-6}$  M whereas solutions of Pcs 17-21 in CH<sub>2</sub>Cl<sub>2</sub> show aggregation at concentrated the redox potentials in the higher concentrated CH<sub>2</sub>Cl<sub>2</sub> solutions used for CV.

Comparative CV measurements on weakly and strongly aggregating Pcs **26** and **19**, respectively, were conducted in pyridine (5–6  $\times$  10<sup>-5</sup> M solutions) to investigate aggregation effects (Table 2). Both pyridine solutions were optically free of aggregates and the first reduction potentials of **26** and **19** both shifted by +0.120 V in comparison to the values obtained in CH<sub>2</sub>Cl<sub>2</sub>. This confirms that differences in aggregation did not affect the measured redox potentials because **26** was not aggregated and **19** was strongly aggregated in the CH<sub>2</sub>Cl<sub>2</sub> solution used for CV. A positive shift of the redox potentials is expected for a change to the donor solvent pyridine<sup>65</sup> although negative shifts have been reported when pyridine strongly coordinates to the central metal ion of a Pc such as Al.<sup>66</sup>

CV measurements on copper(II) Pcs are generally not much affected by aggregation<sup>67</sup> but CV curves of Pcs containing other metal ions may show large changes due to aggregation, such as the splitting of the first reduction wave into two waves.<sup>68</sup> Previous investigations on copper(II) Pcs also established that oxidations and reductions occur solely on the macrocycle and not the copper ion.<sup>27</sup>

Density functional theory (DFT) calculations were performed to gain more insight into the electronic properties. The hybrid density functional UB3LYP<sup>69</sup> with LANL2DZ<sup>70</sup> basis set was chosen for both geometry and property calculations in vacuum because they have been successfully employed in calculations on other copper(II) Pcs.<sup>71</sup> Alkyl groups of Pcs **17–21** and **26** were replaced by methyl groups for DFT calculations to reduce computation time. The statistically preferred  $C_s$ -isomer (50%) was chosen for calculations on Pcs **17–21** and **31** that consist of four different isomers. Comparative calculations on all four isomers of **18** determined a maximum variation in frontier orbital energies of 0.3 eV and in HOMO–LUMO gap of 0.13 eV. Calculated frontier orbital energies of the  $C_s$ - and  $D_{2h}$ -isomers



**Fig. 6** Comparison of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of Pcs **17–21**, **26**, **28**, and **32** determined by CV in CH<sub>2</sub>Cl<sub>2</sub> solution and calculated at the DFT level (UB3LYP/LANL2DZ) (top). Chemical structures of Pcs **28–32** (bottom). Experimental values of **32** were determined by UPS on thin films and  $E_{\text{LUMO}}$  of **28** was calculated from  $E_{\text{HOMO}}$  and the optical gap in pyridine.  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  were calculated from electrochemical measurements by  $E_{\text{HOMO-LUMO}}$  (eV) =  $-[E_{1/2} - (0.48 \text{ V})] - 4.8 \text{ eV} (0.48 \text{ V is the } E_{1/2}^{\text{ox}}$  of ferrocene/ferrocenium (Fc) *vs.* Ag/AgCl).

were 0.2 to 0.3 eV lower than for isomers with  $C_{4h}$  and  $C_{2v}$  symmetry.

A comparison of HOMO and LUMO energies obtained by CV and DFT calculations is given in Fig. 6. Relative changes of  $E_{\rm HOMO}$  and  $E_{\rm LUMO}$  are in good agreement with the values determined by CV, except for **21**, while the absolute values of measured and calculated frontier orbital energies expectedly differ by up to 0.6 eV. Calculated orbital energies were generally lower than the experimental values and differed more for  $E_{\rm HOMO}$ than for  $E_{\rm LUMO}$ . No optimization was attempted, *e.g.* by including solvent interactions, because our interest is the prediction of relative changes.

Values of optical, electrochemical and calculated HOMO– LUMO gaps are compared in Fig. 7. Relative changes were in good agreement for all three methods except for compounds 21 and 26. Calculations predict a decrease in gap for 21 in comparison to 20 but this was not observed experimentally. For compound 26 calculated and electrochemically measured gaps are both slightly larger than for 20 but the optical gap is significantly lower. The HOMO–LUMO gap of the pigment Pc 32 was determined on solid films by UV-Vis spectroscopy and by ultraviolet photoemission spectroscopy (UPS) and are expected to be lower than values in solution.<sup>72</sup>

All calculated HOMO–LUMO gaps are about 0.2–0.3 eV higher than the values obtained by CV and the optical gaps are about 0.2 eV below the electrochemical values. A difference between calculated and experimental values was expected as outlined above and the difference between electrochemical and optical values is in part a solvent effect because the former were determined in pyridine and the latter in CH<sub>2</sub>Cl<sub>2</sub>. A difference in optical and electrochemical HOMO–LUMO gaps of only 0.02 eV was obtained for Pc **26** when both measurements were conducted in CH<sub>2</sub>Cl<sub>2</sub>.

Calculations of orbital energies for Pcs **18** and **31** predict a small difference in energies between the tetra-chlorinated and tetra-fluorinated derivatives as stated earlier. Differences in frontier orbital energies between halide substitution in 2,3- and



2.3

1,4-positions were studied by comparing octa-fluorinated 2,3-subsituted Pc **29** with 1,4-subsituted Pc **30**. The calculated frontier orbital energies of Pc **29** are in excellent agreement with experimental values<sup>63</sup> and a larger HOMO–LUMO gap but lower frontier orbital energies are predicted for Pc **29** in comparison to Pc **30**. This result agrees with comparative optical measurements on other 2,3- and 1,4-substituted Pcs that revealed always larger gaps for 2,3-susbtituted Pcs.<sup>73</sup>

DFT calculations also reveal that the macrocycle and not the substituents predominantly contributes to the HOMO and LUMO orbitals in Pcs **17–31**, which is important for charge conduction along discotic columnar stacks because the transfer integral is less affected by the mutual rotation of stacked macrocycles.<sup>3,53</sup>

#### Conclusions

A change from octa-alkylthio to tetra-alkylthio substitution of discotic Pcs suppresses the formation of tilted columnar phases for aliphatic chains shorter than C8 and the introduction of halide atoms (tetra-alkylthio tetra-halide substitution) also suppresses crystallization. Above room temperature glasses of hexagonal columnar mesophases are accessible by selecting larger halides and/or shorter aliphatic chains as exemplified in Pcs 20 and 22. In contrast, frontier orbital energies and HOMO-LUMO gaps of the discotic Pcs are little affected by a change from octa- to tetra-alkylthio substitution and by the introduction of four Cl, Br, and I atoms. Only the attachment of twelve F-atoms in Pc 17 significantly lowers frontier orbital energies by about 0.5 eV. An  $E_{LUMO}$  of about -4.0 eV places Pc 17 at the border to potentially air stable organic n-type semiconductors but is 0.38 eV higher than  $E_{LUMO}$  of the established n-type semiconductor perfluoro Pc 28. Derivatives of Pc 17 with an  $E_{\rm LUMO}$  well below -4.0 eV may be obtained by the replacement of the thioether groups with electron withdrawing groups such as alkylsulfonyl. However, the comparatively lower thermal and chemical stability of Pc 17 may be detrimental to its application in devices.

# Experimental

#### Methods

UV-Vis spectra of solutions in THF (spectroscopic grade) were recorded on a Varian Cary 50 Conc. UV-Visible Spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were run on Bruker NMR spectrometers (DRX 500 MHz, DPX 300 MHz and DPX 300 MHz with auto-tune). Deuterated chloroform, THF, and pyridine were used as solvents and their residual proton signals functioned as reference signals. Multiplicities of the peaks are given as s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants for 1st-order spin systems are given in Hz. Data are presented in the following order (multiplicity, integration, coupling constant). Fourier transform infrared spectra (FT-IR) were obtained on a Bruker Vector 22. Mass spectrometry measurements were performed by Kirk Green at the Regional Center for Mass Spectrometry and MALDI-MS data were obtained on a Waters/Micromass Micro MX. Some MS measurements were also run on a Finnigan MAT 8222 (DCI), a Bruker TOF (MALDI), a ZAB2-SE-FDP (FD), and an



Applied Biosystems Voyager DE Pro MALDI-TOF with a reflector mirror (N<sub>2</sub> laser at 337 nm). HPLC separations were performed on a Merck-Hitachi-System (L-3000 Photo Diode Array Detector, L-6200A Intelligent Pump, T-6300 Column Thermostat, AS 2000A Autosampler) equipped with 250-4 Merck LiChrospher Si-60 (10  $\mu$ m) and LiChrospher RP-18 (5 $\mu$ m) columns.

Polarized light microscopy was performed on an Olympus TPM51 polarized light microscope that is equipped with a Linkam variable temperature stage HCS410 and digital photographic imaging system (DITO1). Calorimetric studies were performed on a Mettler Toledo DSC 822e and thermal gravimetric analysis was performed on a Mettler Toledo TGA SDTA 851e. Helium (99.99%) was used to purge the system at a flow rate of 60 mL min<sup>-1</sup>. Samples were held at 30 °C for 30 min before heated to 550 °C at a rate of 5 °C min<sup>-1</sup>. All samples were run in aluminium crucibles. A Pfeiffer Vacuum ThermostarTM mass spectrometer (1-300 amu) was attached to the TGA via a thin glass capillary for evolved gas analysis. XRD measurements were run on a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector and GADDS software package. The tube is operated at 40 kV and 40 mA and CuK<sub>a</sub>1 radiation  $(\lambda = 1.54187 \text{ A})$  with an initial beam diameter of 0.5 mm is used. Compound 3 was studied as self-supported bulk material and aligned fibres. Sample detector distances were varied between 15.0 cm and 9.0 cm. A modified Instec hot & cold stage HCS 402 operated via controllers STC 200 and LN2-P (for below ambient temperatures) was used for variable temperature XRD and IR measurements.

Electrochemical measurements were performed using a standard one-compartment, three-electrode electrochemical cell connected to an Electrochemical Analyzer BAS 100B/W (Bioanalytical Systems). The working electrode was a glassy carbon electrode (3 mm diameter) and was freshly polished and ultrasonically rinsed with ethanol before each measurement. Silver (Ag/0.1 M AgNO<sub>3</sub> in CH<sub>3</sub>CN) and platinum wires were used as reference and counter electrodes, respectively. Solvents were obtained from a solvent purification system (Innovative Technology Inc. MA, USA, Pure-Solv 400) and tetrabutylammonium perchlorate (TBAClO<sub>4</sub>) of electrochemical grade was used as supporting electrolyte (Aldrich). Ferrocene (Fluka) functioned as internal standard and all measurements were conducted under dry argon.

DFT calculations were performed with a CAChe WorkSystem Pro Version 6.1 software (Fujitsu America) and with Gaussian 03 (Gaussian, Inc.: Pittsburgh, PA, 2004).

#### Synthesis

Tetrafluorobenzene-1,2-dicarbonitrile 1, 4,5-dichlorobenzene-1,2-dicarbonitrile 2, and 4-nitrobenzene-1,2-dicarbonitrile 5 are commercially available. 4,5-Dibromobenzene-1,2-dicarbonitrile 3, 4,5-diiodobenzene-1,2-dicarbonitrile 4, 4-octylthio-5-chlorobenzene-1,2-dicarbonitrile 7, 4,5-dioctylthio-benzene-1,2-dicarbonitrile 16, Pc 18 and Pc 27 were synthesized following procedures described previously. 4-Octylthio-benzene-1,2-dicarbonitrile 10, 4,5-dihexylthio-benzene-1,2-dicarbonitrile 10, 4,5-dihexylthio-benzene-1,2-dicarbonitrile 14, Pc 21 and Pc 25 have been previously reported but were prepared by different methods. Dimethylimidazolidinone (DMI) and pentanol were dried over molecular sieve 4 Å. Li band was sliced under Ar and used without removal of its Li oxide layer. All other solvents, anhydrous CuCl<sub>2</sub>, Cs<sub>2</sub>CO<sub>3</sub>, and alkylthiols were used without further purification.

**4-Octylthio-3,5,6-trifluorobenzene-1,2-dicarbonitrile (6).** 5.2 g (16.0 mmol) Cs<sub>2</sub>CO<sub>3</sub> were added to a solution of 2.33 g (15.2 mmol) octanethiol and 2.0 g (10.1 mmol) of **1** in 20 mL DMI under stirring and argon at -10 °C. The mixture was stirred for 24 h at -10 °C and then poured into 50 mL 0.1 M aqueous HCl. The product was extracted with DCM (2 × 30 mL) and the combined DCM fractions were extracted with 10% aqueous Na<sub>2</sub>CO<sub>3</sub> solution (2 × 50 mL), with deionized water (3 × 50 mL), and dried over MgSO<sub>4</sub>. Evaporation of the solvent gave a yellow oil that was a mixture of the 4-octylthio- and 4,5-dioctylthio substituted products. Separation by column chromatography on RP-18 using acetonitrile as eluent yielded **6** as yellow oil in 41% yield (1.34 g).

IR (as film on KBr):  $\nu = 2238 \text{ cm}^{-1}$  (C=N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.13 (t, 7.5 Hz, 2H, SCH<sub>2</sub>), 1.62 (m, 2H, CH<sub>2</sub>), 1.42 (m, 2H, CH<sub>2</sub>), 1.27 (m, 8H, CH<sub>2</sub>), 0.87 (t, 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 159.06 (ddd, 259/6/3 Hz, F-C<sub>arom</sub>), 153.17 (ddd, 261/13/6.5 Hz, F-C<sub>arom</sub>), 149.09 (ddd, 266/17/3.5 Hz, F-C<sub>arom</sub>), 125.21 (m, arom.), 116.39 (s, CN), 109.21 (d, 11 Hz, CN), 102.91 and 100.24 (m, arom.), 34.24, 31.73, 29.86, 29.06, 28.94, 28.37, 22.63 (CH<sub>2</sub>), 14.09 (CH<sub>3</sub>). <sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = -21.01 (dd, 9/11 Hz, F<sub>arom</sub>), -37.22 (dd, 9/22 Hz, F<sub>arom</sub>), 51.27 (dd, 11/22 Hz, F<sub>arom</sub>). MS (EI): m/z (%) = 326(19) M<sup>+</sup>, 214(10) M<sup>+</sup>-C<sub>8</sub>H<sub>16</sub>, 57(100). C<sub>16</sub>H<sub>17</sub>F<sub>3</sub>N<sub>2</sub>S (398.31): calculated C, 58.88; H, 5.25; N, 8.58; found C, 59.10; H, 5.45; N, 8.39%.

4-Octylthio-5-bromobenzene-1,2-dicarbonitrile (8), 4-octylthio-5-iodobenzene-1,2-dicarbonitrile (9), 4-octylthiobenzene-1,2dicarbonitrile (10), 4-pentylthio-5-chlorobenzene-1,2-dicarbonitrile (11) and 4-pentylthiobenzene-1,2-dicarbonitrile (12). Cs<sub>2</sub>CO<sub>3</sub> (16.0 mmol, 5.20 g) were added to a solution of octanethiol (15.2 mmol, 2.22 g) or pentanethiol (15.2 mmol, 1.58 g) and 10.1 mmol of 3 (2.88 g), 4 (3.84 g), or 5 (1.75 g) in 20 mL of DMI under argon. The mixture was stirred for 2 d at 50 °C, cooled to room temperature, and added to 50 mL 0.1 M aqueous HCl. A vellow precipitate was filtered off, washed with 10% aqueous Na<sub>2</sub>CO<sub>3</sub> solution (2  $\times$  50 mL), with deionized water (3  $\times$ 50 mL), and dried in vacuum. Recrystallization from hexane gave pale yellow solids. The crude reaction mixtures of 8, 9, and 11 also contained the dialkylthio substituted derivatives in about 20 mol% according to 1H NMR. Recrystallization from diisopropylether gave fractions of 8, 9, and 11 with a content >90 mol%, which were further purified by column chromatography on silica gel using isopropylether-hexane as eluent. Pure 8, 9, and 11 were isolated as pale yellow solids in 62% (2.18 g), 70%(2.82 g), and 55% (1.47g), respectively. Compounds 10 and 12 were purified by column chromatography on silica gel using isopropylether-hexane 1: 2 as eluent to give the pure products as white crystalline powders in yields of 84% (2.30 g) and 89% (2.07 g), respectively.

Compound 8: mp = 77 °C. IR (as film on KBr):  $\nu$  = 2229 cm<sup>-1</sup> (C=N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.89 (s, 1H, arom.), 7.40 (s, 1H, arom.), 2.99 (t, 7.4 Hz, 2H, SCH<sub>2</sub>), 1.78 (m, 2H, CH<sub>2</sub>), 1.48 (m, 2H, CH<sub>2</sub>), 1.34–1.28 (m, 8H, CH<sub>2</sub>), 0.89 (t, 7.0 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 149.64 (arom.), 136.82 (arom.), 128.70 (arom.), 126.29 (arom.), 115.38 (arom.), 115.29 (arom.), 114.81 (CN), 111.28 (CN), 32.96, 32.12, 29.44, 29.41, 29.30, 27.97, 23.00 (CH<sub>2</sub>), 14.46 (CH<sub>3</sub>). MS (EI): *m*/*z* (%) = 352(25) M<sup>+</sup>, 240(24) M<sup>+</sup>-C<sub>8</sub>H<sub>16</sub>, 112(7) C<sub>8</sub>H<sub>16</sub><sup>+</sup>, 43(100). C<sub>16</sub>H<sub>19</sub>BrN<sub>2</sub>S (351.31): calculated C, 54.70; H, 5.45; N, 7.97; found C, 54.59; H, 5.57; N, 7.80%.

Compound **9**: mp = 86 °C. IR (as film on KBr):  $\nu$  = 2230 cm<sup>-1</sup> (C $\equiv$ N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.13 (s, 1H, arom.), 7.33 (s, 1H, arom.), 2.99 (t, 7.3 Hz, 2H, SCH<sub>2</sub>), 1.79 (m, 2H, CH<sub>2</sub>), 1.51 (m, 2H, CH<sub>2</sub>), 1.35–1.28 (m, 8H, CH<sub>2</sub>), 0.89 (t, 6.7 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 152.96 (arom.), 143.29 (arom.), 127.58 (arom.), 115.95 (arom.), 115.58 (arom.), 114.63 (CN), 111.08 (CN), 101.82 (I-C<sub>arom</sub>), 34.24, 32.12, 29.44, 29.42, 29.33, 27.89, 23.01 (CH<sub>2</sub>), 14.48 (CH<sub>3</sub>). MS (EI): *m/z* (%) = 398(66) M<sup>+</sup>, 286(49) M<sup>+</sup>-C<sub>8</sub>H<sub>16</sub>, 112(8) C<sub>8</sub>H<sub>16</sub><sup>+</sup>, 43(100). C<sub>16</sub>H<sub>19</sub>IN<sub>2</sub>S (398.31): calculated C, 48.25; H, 4.81; N, 7.03; found C, 48.43; H, 5.06; N, 6.86%.

Compound **10**: mp = 36 °C. IR (as film on KBr):  $\nu$  = 2228 cm<sup>-1</sup> (C=N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.63 (d, 8.3 Hz, 1H, arom.), 7.55 (d, 2.0 Hz, 1H, arom.), 7.48 (dd, 8.3, 2.0 Hz, 1H, arom.), 3.00 (t, 7.3 Hz, 2H, SCH<sub>2</sub>), 1.72 (m, 2H, CH<sub>2</sub>), 1.46 (m, 2H, CH<sub>2</sub>), 1.32–1.28 (m, 8H, CH<sub>2</sub>), 0.89 (t, 6.7 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 147.92 (arom.), 133.53 (arom.), 130.33 (arom.), 130.21 (arom.), 116.63 (arom.), 115.96 (arom.), 115.59 (CN), 111.01 (CN), 32.26, 32.12, 29.47, 29.40, 29.19, 28.55, 23.00 (CH<sub>2</sub>), 14.46 (CH<sub>3</sub>). MS (EI): *m*/*z* (%) = 272(100) M<sup>+</sup>, 160(53) M<sup>+</sup>-C<sub>8</sub>H<sub>16</sub>.

Compound **11**: mp = 135 °C. IR (as film on KBr):  $\nu$  = 2229 cm<sup>-1</sup> (C $\equiv$ N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.70 (s, 1H, arom.), 7.45 (s, 1H, arom.), 2.99 (t, 8.4 Hz, 2H, SCH<sub>2</sub>), 1.78 (m, 2H, CH<sub>2</sub>), 1.58–1.31 (m, 4H, CH<sub>2</sub>), 0.94 (t, 7.5 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 147.3 (arom.), 136.0 (arom.), 133.1 (arom.), 128.6 (arom.), 114.8 (arom.), 114.5 (arom.), 114.4 (CN), 110.9 (CN), 31.9, 30.9, 27.3, 22.1 (CH<sub>2</sub>), 13.8 (CH<sub>3</sub>). C<sub>13</sub>H<sub>13</sub>ClN<sub>2</sub>S (264.78): calculated C, 58.97; H, 4.95; N, 10.58; found C, 59.09; H, 5.17; N, 10.36%.

Compound **12**: mp = 53 °C. IR (as film on KBr):  $\nu$  = 2228 cm<sup>-1</sup> (C $\equiv$ N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.64 (d, 8.1 Hz, 1H, arom.), 7.55 (d, 1.8 Hz, 1H, arom.), 7.46 (dd, 8.1 Hz, 1.9 Hz, 1H, arom.), 3.01 (t, 7.0 Hz, 2H, SCH<sub>2</sub>), 1.73 (m, 2H, CH<sub>2</sub>), 1.49–1.35 (m, 4H, CH<sub>2</sub>), 0.93 (t, 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 147.6 (arom.), 133.2 (arom.), 130.1 (arom.), 129.9 (arom.), 116.3 (arom.), 115.6 (arom.), 115.2 (CN), 110.7 (CN), 31.9 (CH<sub>2</sub>), 30.9 (CH<sub>2</sub>), 27.9 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>), 13.9 (CH<sub>3</sub>). MS (EI): *m/z* (%) = 230(100) M<sup>+</sup>, 160(41) M<sup>+</sup>-C<sub>5</sub>H<sub>10</sub>. C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>S (230.33): calculated C, 58.97; H, 4.95; N, 10.58; found C, 58.81; H, 4.99; N, 10.44%.

4,5-Dipentylthio-benzene-1,2-dicarbonitrile (13), 4,5-dihexylthio-benzene-1,2-dicarbonitrile (14), 4,5-diheptylthio-benzene-1,2-dicarbonitrile (15).  $Cs_2CO_3$  (25.0 mmol, 8.13 g) was added to a solution of alkylthiol (25.0 mmol) and 2 (10.1 mmol, 2.00 g) in 20 mL of DMI under argon. The mixture was stirred for 2 d at 50 °C, cooled to room temperature, and added to 50 mL 0.1 M aqueous HCl. A yellow precipitate was filtered off, washed with 10% aqueous Na<sub>2</sub>CO<sub>3</sub> solution (2 × 50 mL), with deionized water (3 × 50 mL), and dried in vacuum. Recrystallization from

hexane gave pale yellow solids. The crude reaction mixtures of **13**, **14**, and **15** were purified by column chromatography on silica gel using isopropylether–hexane mixtures as eluent. Compounds **13**, **14**, and **15** were obtained as pale yellow solids in yields of 58% (1.95 g), 64% (2.33 g), and 67% (2.63 g), respectively.

Compound **13**: mp = 67 °C. IR (as film on KBr):  $\nu$  = 2229 cm<sup>-1</sup> (C $\equiv$ N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.40 (s, 2H, arom.), 3.01 (t, 7.2 Hz, 4H, SCH<sub>2</sub>), 1.75 (m, 4H, CH<sub>2</sub>), 1.5–1.3 (m, 8H, CH<sub>2</sub>), 0.92 (t, 7.1 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 144.3 (arom.), 128.2 (arom.), 115.8 (arom.), 111.2 (CN), 32.8, 31.1, 27.9, 22.3, 14.0 (CH<sub>3</sub>). C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub> (332.53): calculated C, 65.02; H, 7.27; N, 8.42; found C, 65.09; H, 7.34; N, 8.36%.

Compound **14**: mp = 71 °C. IR (as film on KBr):  $\nu$  = 2228 cm<sup>-1</sup> (C $\equiv$ N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.40 (s, 2H, arom.), 3.01 (t, 7.2 Hz, 4H, SCH<sub>2</sub>), 1.74 (m, 4H, CH<sub>2</sub>), 1.48 (m, 4H, CH<sub>2</sub>), 1.3–1.2 (m, 8H, CH<sub>2</sub>), 0.89 (t, 6.9 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 144.3 (arom.), 128.2 (arom.), 115.8 (arom.), 111.1 (CN), 32.8, 31.4, 28.7, 28.1, 22.6, 14.1 (CH<sub>3</sub>).

Compound **15**: mp = 61 °C. IR (as film on KBr):  $\nu$  = 2229 cm<sup>-1</sup> (C $\equiv$ N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.40 (s, 2H, arom.), 3.01 (t, 7.2 Hz, 4H, SCH<sub>2</sub>), 1.74 (m, 4H, CH<sub>2</sub>), 1.48 (m, 4H, CH<sub>2</sub>), 1.29 (m, 12H, CH<sub>2</sub>), 0.89 (t, 7.0 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 144.3 (arom.), 128.2 (arom.), 115.8 (arom.), 111.1 (CN), 32.8, 31.7, 29.0, 28.9, 28.2, 22.7, 14.2 (CH<sub>3</sub>). C<sub>22</sub>H<sub>32</sub>N<sub>2</sub>S (388.63): calculated C, 67.99; H, 8.30; N, 7.21; found C, 68.10; H, 8.39; N, 7.16%.

Preparation of copper(II)-2,9,16,23 (and 2,10,17,24; 2,10,16,24; 2,9,17,24)-tetraoctylthio-1,3,4,8,10,11,15,17,18,22,24,25 (and 1,3,4,8,9,11,15,16,18,22,23,25; 1,3,4,8,9,11,15,17,18,22,23,25; 1,3,4,8,10,11,15,16,18,22,23,25)-dodecafluorophthalocyaninato (17). Compound 6 (1.8 mmol, 600 mg), anhydrous CuCl<sub>2</sub> (1.8 mmol, 247 mg) and quinoline (3 mL filtered through activated Al<sub>2</sub>O<sub>3</sub>) were added into a glass tube in a glove box. The glass tube was removed from the glove box, flame sealed, and heated to 180 °C for 20 h. The reaction mixture was suspended in toluene (15 mL), extracted with 0.01 M HCl ( $4 \times 10$  mL), washed with water and dried over MgSO<sub>4</sub>. The crude product was further purified by column chromatography on silica gel with toluene as solvent. The toluene fraction containing the product was concentrated and 11 was precipitated out by the addition of acetone to yield 150 mg (0.11 mmol, 24%)

Compound **17**: IR (as film on KBr):  $\nu = 1600 \text{ cm}^{-1}$ (C=C<sub>arom</sub>). MS (MALDI-TOF, sinapinic acid, positive): m/z =1367 M<sup>+</sup>. C<sub>64</sub>H<sub>68</sub>N<sub>8</sub>S<sub>4</sub>F<sub>12</sub>Cu (1369.07): calculated C, 56.15; H, 5.01; N, 8.18; found C, 56.47; H, 5.18; N, 7.96%.

General synthetic procedure for the preparation of copper(II)-2,9,16,23 (and 2,10,17,24; 2,10,16,24; 2,9,17,24)-tetrabromo-3,10,17,24 (and 3,9,16,23; 3,9,17,23; 3,10,16,23)-tetraoctylth-iophthalocyaninato (19), copper(II)-2,9,16,23 (and 2,10,17,24; 2,10,16,24; 2,9,17,24)-tetraiodo-3,10,17,24 (and 3,9,16,23; 3,9,17,23; 3,10,16,23)-tetraoctylthiophthalocyaninato (20), copper(II)-2,9,16,23 (and 2,10,17,24; 2,10,16,24; 2,9,17,24)-tetraoctylthiophthalocyaninato (21), copper(II)-2,9,16,23 (and 2,10,17,24; 2,10,16,24; 2,9,17,24)-tetrachloro-3,10,17,24 (and 3,9,16,23; 3,9,17,23; 3,10,16,23)-tetrapentylthiophthalocyaninato (22), and

copper(II)-2,9,16,23 (and 2,10,17,24; 2,10,16,24; 2,9,17,24)-tetrapentylthiophthalocyaninato (23). Compounds 8, 9, 10, 11 or 12 (2.0 mmol) were dissolved in 20 cm<sup>3</sup> of dry 1-pentanol and heated to reflux under argon. Lithium (2.88 mmol, 20 mg) was added to the stirred solutions and the reactions were kept under reflux for 2 h and then cooled to 60 °C. 30 cm<sup>3</sup> of acetic acid were added and the dark solutions were stirred for 1 h at 60 °C. The suspensions were cooled to 4 °C and the precipitated metal-free Pcs were filtered off. The obtained crude Pcs were metallated in a solution of copper(II) acetate (about 6 mmol) in THF at 50 °C for about 5 h. Progress of the metallation was monitored by UV-Vis spectroscopy. Addition of methanol at rt precipitated the copper Pcs and they were again precipitated from diethoxymethane solution by the addition of acetone. Silica gel flash chromatography using toluene-n-hexane mixtures as eluent yielded 19, 20, 21, 22, and 23 in 54% (396 mg), 48% (398 mg), 62% (357 mg), 55% (308 mg), and 66% (325 mg), respectively.

Compound **19**: IR (as film on KBr):  $\nu = 1598 \text{ cm}^{-1}$ (C=C<sub>arom</sub>). MS (MALDI-TOF, sinapinic acid, positive): m/z =1468 M<sup>+</sup>. C<sub>64</sub>H<sub>76</sub>N<sub>8</sub>S<sub>4</sub>Br<sub>4</sub>Cu (1468.79): calculated C, 52.34; H, 5.22; N, 7.63; found C, 52.70; H, 5.28; N, 7.51%.

Compound **20**: IR (as film on KBr):  $\nu = 1596 \text{ cm}^{-1}$ (C=C<sub>arom.</sub>). MS (MALDI-TOF, sinapinic acid, positive):  $m/z = 1656 \text{ M}^+$ . C<sub>64</sub>H<sub>76</sub>N<sub>8</sub>S<sub>4</sub>l<sub>4</sub>Cu (1656.79): calculated C, 46.40; H, 4.62; N, 6.76; found C, 46.54; H, 4.80; N, 6.59%.

Compound **21**: IR (as film on KBr):  $\nu = 1602 \text{ cm}^{-1}$ (C=C<sub>arom.</sub>). MS (MALDI-TOF, sinapinic acid, positive): m/z =1153 M<sup>+</sup>. C<sub>64</sub>H<sub>80</sub>N<sub>8</sub>S<sub>4</sub>Cu (1153.21): calculated C, 66.66; H, 6.99; N, 9.72; found C, 67.03; H, 7.08; N, 9.55%.

Compound **22**: IR (as film on KBr):  $\nu = 1598 \text{ cm}^{-1}$ (C=C<sub>arom.</sub>). MS (MALDI-TOF, sinapinic acid, positive): m/z =1122 M<sup>+</sup>. C<sub>52</sub>H<sub>52</sub>Cl<sub>4</sub>N<sub>8</sub>S<sub>4</sub>Cu (1122.64): calculated C, 55.63; H, 4.67; N, 9.98; found C, 55.79; H, 4.82; N, 9.71%.

Compound **23**: IR (as film on KBr):  $\nu = 1601 \text{ cm}^{-1}$ (C=C<sub>arom.</sub>). MS (MALDI-TOF, sinapinic acid, positive): m/z =984 M<sup>+</sup>. C<sub>52</sub>H<sub>56</sub>N<sub>8</sub>S<sub>4</sub>Cu (984.86): calculated C, 66.66; H, 6.99; N, 9.72; found C, 67.03; H, 7.08; N, 9.55%.

General synthetic procedure for the preparation of copper(II)-2,3,9,10,16,17,23,24-octapentylthiophthalocyaninato (24), copper(II)-2,3,9,10,16,17,23,24-octahexylthiophthalocyaninato (25), copper(II)-2,3,9,10,16,17,23,24-octaheptylthiophthalocyaninato

(26). Lithium (28.8 mmol, 200 mg) was added to 1-octanol (5 mL) and stirred under Ar at 90 °C for 12 h to ensure a complete conversion of lithium octanolate. Compound 13, 14, or 15 (1.0 mmol) was added to these slurries and stirred at 90 °C for 3 d. Acetic acid (10 mL) was added in portions to the reaction mixtures at 60 °C and the obtained suspensions were cooled to 4 °C. The precipitated metal-free Pcs were filtered off, re-dissolved in THF (10 mL) and metallated with copper(II) acetate (about 4 mmol) at 50 °C. Metallation was monitored by UV-Vis spectroscopy and completed after 4–5 h. Addition of methanol precipitated the crude copper Pcs that were further purified by silica gel flash chromatography using toluene–*n*-hexane 8 : 2 as eluent. Pcs 24, 25, and 26 were obtained in 70% (243 mg), 66% (248 mg), and 69% (279 mg) yield.

Compound 24: IR (as film on KBr):  $\nu = 1599 \text{ cm}^{-1}$ (C=C<sub>arom</sub>). MS (MALDI-TOF, sinapinic acid, positive):  $m/z = 1391 \text{ M}^+$ . C<sub>72</sub>H<sub>96</sub>N<sub>8</sub>S<sub>8</sub>Cu (1393.65): calculated C, 62.05; H, 6.94; N, 8.04; found C, 62.30; H, 7.18; N, 7.79%.

Compound **25**: IR (as film on KBr):  $\nu = 1600 \text{ cm}^{-1}$ (C=C<sub>arom.</sub>). MS (MALDI-TOF, sinapinic acid, positive):  $m/z = 1504 \text{ M}^+$ . C<sub>80</sub>H<sub>112</sub>N<sub>8</sub>S<sub>8</sub>Cu (1505.86): calculated C, 63.81; H, 7.50; N, 7.44; found C, 64.00; H, 7.68; N, 7.21%.

Compound **26**: IR (as film on KBr):  $\nu = 1598 \text{ cm}^{-1}$ (C=C<sub>arom</sub>). MS (MALDI-TOF, sinapinic acid, positive):  $m/z = 1616 \text{ M}^+$ . C<sub>88</sub>H<sub>128</sub>N<sub>8</sub>S<sub>8</sub>Cu (1618.08): calculated C, 65.32; H, 7.97; N, 6.93; found C, 65.54; H, 8.08; N, 6.73%.

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