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Large Faraday Rotation in Optical-Quality Phthalocyanine and **Porphyrin Thin Films**

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day rotation involves the rotation of plane-polarized light as it passes through an optical medium in the presence of an external magnetic field oriented parallel to the direction of light propagation. Faraday rotators find applications in optical isolators and magnetic-field imaging technologies. In recent years, organic thin films comprised of polymeric and small-molecule chromophores have demonstrated Verdet constants, which measure the magnitude of rotation at a given magnetic field strength and material thickness, that exceed those found in conventional inorganic crystals. We report herein the thin-film magnetic circular birefringence (MCB) spectra and maximum Verdet constants of several commercially available and newly synthesized phthalocya-



nine and porphyrin derivatives. Five of these species achieved maximum Verdet constant magnitudes greater than $10^5 \text{ deg } \text{T}^{-1} \text{ m}^{-1}$ at wavelengths between 530 and 800 nm. Notably, a newly reported zinc(II) phthalocyanine derivative (ZnPc-OT) reached a Verdet constant of -33×10^4 deg T⁻¹ m⁻¹ at 800 nm, which is among the largest reported for an organic material, especially for an opticalquality thin film. The MCB spectra are consistent with resonance-enhanced Faraday rotation in the region of the Q-band electronic transition common to porphyrin and phthalocyanine derivatives, and the Faraday A-term describes the electronic origin of the magneto-optical activity. Overall, we demonstrate that phthalocyanines and porphyrins are a class of rationally designed magnetooptical materials suitable for applications demanding large Verdet constants and high optical quality.

INTRODUCTION

When plane-polarized light passes through any optically transparent material in the presence of a magnetic field oriented parallel to the direction of propagation, the plane of polarization will rotate. This magneto-optical phenomenon is known synonymously as magneto-optical rotation (MOR) and the Faraday effect, and is caused by magnetically induced circular birefringence (MCB). It may be described empirically by the equation below.

$$\varphi = VBd \tag{1}$$

Here, the magnitude of the rotation φ of plane-polarized light is proportional to the strength of the magnetic field *B*, the path length d, and the wavelength-dependent Verdet constant V (Figure 1a). Several key magneto-optical technologies rely on materials with large Verdet constants, including optical isolators crucial to our telecommunication infrastructure^{1,2} and magneto-optical imaging devices used in aircraft fuselage inspection.^{3,4} The development of materials with larger Verdet constants may lead to lighter, less expensive, and more sensitive instruments.

The inorganic material terbium gallium garnet (TGG) exhibits a large Verdet constant across the visible and nearinfrared (IR) spectrum, from -1.0×10^4 deg T⁻¹ m⁻¹ at 532 nm to $-0.3 \times 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$ at 980 nm,⁵ and is considered the benchmark for Faraday materials.⁶ Although the high optical quality, high laser damage threshold, and low absorptivity of TGG and other inorganic crystals make them ideal for many applications, future magneto-optical technologies may demand the lightness, flexibility, tunability, and processability that are characteristics of many organic materials. Over the past decade, several organic materials have matched or exceeded the magneto-optical performance of TGG by employing a variety of design strategies, including extended conjugation,^{5,7-9} helical chromophores,^{10,11} the inclusion of paramagnetic dopants,¹²⁻¹⁶ and spin-forbidden transitions.¹⁷ To date, the largest Verdet constants reported in organic thin-films are on the order of $10^5 \text{ deg } \text{T}^{-1} \text{ m}^{-1}$.^{7,11,18} However, many high-performance organic Faraday rotators are not of optical quality because they incorporate light-scattering

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Figure 1. (a) Illustration of the principle of Faraday rotation from a thin film. (b) The characteristic line shape of the Faraday A-Term for an arbitrary electronic transition. (c) The main orbital transitions contributing to the Faraday rotation in the porphyrin and phthalocyanine Q-band are from the HOMO to degenerate LUMOs. (TD-DFT: ω B97X-D/6-31G*).

nanoparticles¹⁴ or crystalline domains.¹⁸ Verdet constants in optical-quality organic thin films beyond 10⁴ deg T⁻¹ m⁻¹ are key to realizing low cost and high sensitivity magneto-optical imaging and future sensing technologies.

One under-explored route to achieve optical-quality organic thin films with large Verdet constants leverages the phenomenon of resonance-enhanced Faraday rotation in certain small-molecule chromophores. The quantum-mechanical underpinnings of Faraday rotation enhancement near optical transitions are well described by the equations of Buckingham and Stephens.¹⁹ These equations may be broken down into three independent terms, the A-, B-, and C-terms, which when summed are directly proportional to the Verdet constant at a given wavelength. In diamagnetic organic materials, the A-term (eq 2) often dominates and guides the analysis reported in this investigation.

$$A(j \leftarrow n) = \frac{3}{d_n} \sum_{n} \left[\langle j | m_z | j \rangle - \langle n | m_z | n \rangle \right] \operatorname{Im} \{ \langle n | \mu_x | j \rangle \langle j | \mu_y | n \rangle \}$$
(2)

In eq 2, the magnitude of the A-term for a transition from electronic state $j \leftarrow n$ is denoted, where d_n is the degeneracy of the ground electronic states, \sum_n is the sum over all degenerate transitions, m_z is the magnetic dipole moment operator parallel

to the incident light beam, μ_x and μ_y are the electric dipole moment operators perpendicular to the beam, and Im is the function which returns the imaginary component of a complex number. If the excited state is degenerate, then the expression must be summed over all degenerate transitions $j \leftarrow n$. The characteristic A-term line shape is shown in Figure 1b. Crucially, the A-term only arises in electronic transitions which involve degenerate electronic states that undergo magnetic field induced Zeeman splitting.

In organic chromophores in the visible and near-IR regions, degenerate electronic states are mostly limited to high-symmetry molecules with degenerate frontier molecular orbitals. The optical transition denoted as the Q-band found in porphyrins and phthalocyanines fulfills this requirement as a result of the degeneracy of the LUMOs (Figure 1c), which lead to degenerate excited states of ${}^{1}E_{u}$ symmetry and a non-degenerate ground state of ${}^{1}A_{1g}$ symmetry. From eq 2, the magnitude of the Faraday A-term for the Q-band transition may be expressed as the product of isotropic reduced matrix elements, as shown by Barron.²⁰

$$A({}^{1}E \leftarrow {}^{1}A_{1}) = -\frac{i}{2\sqrt{2}} \langle {}^{1}E \parallel m \parallel {}^{1}E \rangle |\langle {}^{1}A_{1} \parallel \mu \parallel {}^{1}E \rangle |^{2}$$
(3)

The first term is the isotropic reduced magnetic moment of the ${}^{1}E_{u}$ excited state, and the second term is the isotropic transition dipole strength. Such analysis has been used for decades in the interpretation of solution-state magnetic circular dichroism (MCD) spectra of phthalocyanines and porphyrins.^{21,22} However, MCB spectra for these species is rarely measured in the solution state,^{23,24} and to our knowledge, the Faraday rotation has not been evaluated in the solid state, especially in the context of thin-film devices. In this contribution, we establish porphyrin and phthalocyanine chromophores as a class of high-performance magneto-optical materials with large Verdet constants in optical-quality thin films.

MATERIALS AND METHODS

The synthetic routes to phthalocyanine derivatives ZnPc-OT, ZnPc- $(\mathbf{R})/(\mathbf{rac})/(\mathbf{S})$, and $\mathbf{CuPc}-(\mathbf{R})/(\mathbf{rac})/(\mathbf{S})$, as well as terbium doubledecker phthalocyanine TbPc₂-(rac) are shown in Figure 2. The bisthianthrene phthalonitrile (1) precursor to ZnPC-OT was obtained from the addition of 1,2-dimercapto benzene to tetrafluorophthalonitrile as previously reported.²⁵ The templated cyclization of 1 then proceeded under standard conditions²⁶ to give ZnPc-OT in modest overall yields. Bisalkoxy phthalonitrile (4) was synthesized in a manner similar to previous reports;²⁷ however, synthesis of the (R)-enantiomer (4-(R)) is reported for the first time. In brief, the alkylation of catechol by enantiopure bromo-alkanes derived from citronellol gave bisalkoxybenzene 2, which was then brominated twice to give 3. Cyanation of 3 was accomplished by the Rosemund-von Braun reaction, giving bis-alkoxy phthalonitrile 4. Phthalocyanine derivatives ZnPc-(R)/(rac)/(S) and CuPc-(R)/(S)(rac)/(S) were obtained from 4 via templated cyclization in a manner analogous to previously reported procedures.28 Terbium double-decker phthalocyanine TbPc2-(rac) only differs from wellprecedented species by the identity of the alkyl side chains and was synthesized from 4-(rac) in an analogous manner.²⁹ Subpthalocyanine SubPc was obtained following previously reported procedures. Zinc(II) tetraphenylporphyrin (ZnTPP) and ruthenium(II) tetraphenylporphyrin carbonyl (RuTPP) were used as received from Sigma-Aldrich. See the Supporting Information for detailed synthetic methods.

Thin films were prepared by being spin-coated onto thin $(170 \pm 5 \ \mu m)$ glass substrates from concentrated chloroform solutions $(10-20 \ \mu m)$



Figure 2. Synthetic routes to novel phthalocyanine derivatives (a) octathianthrene-substituted zinc pththalocyanine (ZnPc-OT), (b) bisalkyloxy phthalonitrile (4), and (c) Zn- and Cu-phthalocyanines (ZnPc-(rac)/(R)/(S) and CuPc-(rac)/(R)/(S)) and Tb-double-decker phthalocyanine ($TbPc_2-(rac)$).

mg mL⁻¹) at a rate of 1000 rpm. Only samples of high optical quality were measured, as evidenced by polarized optical microscopy images (Leica DMRXP) taken of the thin films in transmission (Figure S1). The thickness of each thin film was determined using contact profilometry (Dektak 6 M Profilometer) or atomic force microscopy (Nanoscope V with Dimension 3100) and ranged from 65 to 320 nm. Thermal annealing was conducted using a Linkam TMS 94 hot stage with the following temperature profile: heated from room temperature to 150 °C at 30 °C min⁻¹ and then cooled to room temperature at 1 $^{\circ}\text{C}$ min $^{-1}$ under an ambient atmosphere. MCB and UV–vis spectra were obtained from a home-built measurement system based on established designs.^{14,17,31} At each wavelength, the magnitude and sign of the rotation of plane polarized light was measured at five different magnetic field strengths ranging from -0.5 to 0.5 T to ensure a linear response consistent with eq 1. The performance of the system was validated using reference samples of BK7 glass and TGG, giving values consistent with those found in the literature.⁵ The spectrometer is fully described in the Supporting Information.

RESULTS AND DISCUSSION

Two metal tetraphenylporphyrin (TPP) derivatives, zinc(II) tetraphenylporphyrin (**ZnTPP**) and ruthenium(II) tetraphenylporphyrin carbonyl (**RuTPP**), produced optical-quality thin films and also displayed large Verdet constants (Figure 3). Other metal tetraphenylporphyrin derivatives were screened, but these either did not form optical quality films as a result of crystallization or poor surface coverage (nickel(II) tetraphenylporphyrin and metal-free tetrakis(pentafluorophenyl)-porphyrin), or their apparent Verdet constants were below the detection limit of our instrument (ca. 1×10^4 deg T⁻¹ m⁻¹ for ~100 nm thin films) in the region of the Q-band

(cobalt(II) tetraphenylporphyrin, iron(III) tetraphenylporphyrin chloride, and metal-free tetraphenylporphyrin). The MCB and UV-vis spectra of thin films of ZnTPP and RuTPP showed large magneto-optical responses in the Q-band region (Figure 3). The maximum absolute value of the Verdet constant for both species was achieved at the wavelength corresponding to maximum absorbance, reaching -6×10^4 deg T⁻¹ m⁻¹ at 560 nm for ZnTPP and -24×10^4 deg T⁻¹ m^{-1} at 530 nm for **RuTPP**. The characteristic line shape of the Faraday A-term (cf. Figure 1b) was observed most clearly in the RuTPP thin film. The more complex line shape observed in the ZnTPP thin film may be attributed to overlapping Aterm contributions from vibrational replicas of the Q-band, which were also observed in the solution state MCB spectrum (Figure S6a). Thermal annealing to 150 °C had little effect on the magnitude or line shape of the Verdet constant spectra of RuTPP and ZnTPP thin films (Figure S3a,b), although the optical quality of the ZnTPP thin film was lowered due to the formation of scattering crystalline domains (Figure S4b). The figure-of-merit (FOM), defined as the magnitude of the Faraday rotation (deg T^{-1}) divided by the absorbance (unitless) at a given wavelength, reached 0.052 deg T^{-1} in RuTPP thin films. Although this FOM value is smaller than is observed in many inorganic crystals such as TGG, the larger Verdet constant and fabrication advantages of RuTPP make it an especially attractive material in technologies in which the use of short optical path lengths minimize absorption, such as magneto-optical imaging.

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Figure 3. (a) Chemical structures and Faraday rotation and absorbance spectra of (b) ZnTPP and (c) RuTPP thin films.

The subphthalocyanine derivative **SubPc** also formed optical quality thin films when it was spin-coated from concentrated chloroform solutions. The solubility of **SubPc** and the optical clarity of its thin films were enhanced by the inclusion of bulky thioarene solubilizing groups (Figure 4a). These films achieved a maximum Verdet constant of -11×10^4 deg T⁻¹ m⁻¹ at 650 nm and displayed the characteristic A-term line shape centered at the subphthalocyanine Q-band transition (Figure 4b). Neither the Faraday rotation nor the optical quality of **SubPc** thin films were impacted when thermally annealed (Figures S3c and S4c). Although subphthalocyanine derivatives are of



Figure 4. (a) Chemical structure and (b) Faraday rotation and absorbance spectra of a SubPc thin film.

lower symmetry (C_{3v}) than their phthalocyanine and porphyrin counterparts (D_{4h} generally), they contain formally degenerate frontier molecular orbitals similar to those found in metal porphyrins (Figure S13).³² This leads to the analogous electronic state diagrams in subphthalocyanines, resulting in comparable Faraday rotation.

The synthetic flexibility of the phthalocyanine core structure enabled us to study the effects of side-chain chirality and the presence of paramagnetic metal centers on the magneto-optical performance of their thin films. Previous studies of Faraday rotation have demonstrated the impact of appended chiral side chains in organic thin-film magneto-optical materials on both the sign and magnitude of the Faraday rotation; however, the magneto-optical responses of these systems were not attributed to Faraday A-term mechanisms.^{10,11,17} As shown in Figure 5a– b, for ZnPc and CuPc derivatives, the line shape of the MCB spectrum in the region surrounding the Q-band is consistent with a Faraday A-term. However, the appended chiral side chains had little effect on the magnitude, line shape, or sign of the Faraday rotation of diamagnetic zinc(II) phthalocyanine derivatives ZnPc-(R), ZnPc-(S), and ZnPc-(rac). The largest apparent effect is found in minor variations in the Verdet constant maxima, which range from $-9.0 \times 10^4 \text{ deg } \text{T}^{-1} \text{ m}^{-1}$ in **ZnPc-(S)** to $-15.2 \times 10^4 \text{ deg } \text{T}^{-1} \text{ m}^{-1}$ in **ZnPc-(R)** at 640 nm. The effect of chiral side chain substitution was also small in copper(II) phthalocyanine derivatives CuPc-(R), CuPc-(S), and CuPc-(rac), ranging from $-6.2 \times 10^4 \text{ deg } \text{T}^{-1} \text{ m}^{-1}$ in CuPc-(rac) to $-10.6 \times 10^4 \text{ deg } \text{T}^{-1} \text{ m}^{-1}$ in CuPc-(S) at 630 nm. Thermal annealing of ZnPc-(R), ZnPc-(S), and ZnPc-(rac) thin films induced partial crystallization as evidenced by polarized optical microscopy (Figure S4d-f). As a result, the



Figure 5. Faraday rotation and absorbance spectra of (a) ZnPc-(R)/(S)/(rac), (b) CuPc-(R)/(S)/(rac), (c) $TbPc_2-(rac)$, and (d) ZnPc-OT thin films.

optical quality of the thin films was lowered, and the maximum Verdet constants decreased to $-4.4-9.9 \times 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$ (Figure S3d-f). Overall, the effect of thermal annealing on the MO activity was consistent between the enantiomers and the racemic mixture. These results suggest that remote chirality (via side chain introduction) does not strongly contribute to Faraday rotation in materials in which the Faraday A-term dominates. Presumably, the perturbation of the π and π^* molecular orbitals which contribute to the Faraday A-term (Figure 1c) by the remote chiral centers is small. Additionally, the Faraday A-term mechanism is thought to be insensitive to chirality, and any MO activity resulting from magnetochiral dichroism (MChD) or birefringence (MChB) should be both small and not detectable with the spectrometer used in this experiment.²⁰

Substitution of a diamagnetic metal ion with a paramagnetic metal ion at the center of phthalocyanine allowed us to study the impact of spin magnetic moments due to unpaired electrons on the magneto-optical properties of phthalocyanine thin films. Studies of Faraday rotation in other organic thin films have suggested that the presence of paramagnetic species enhances the magneto-optical activity of adjacent polymeric chromophores.^{11,12} The substitution of diamagnetic zinc(II) with paramagnetic copper(II) had little effect on the magnitude of the Faraday rotation as demonstrated in Figure 5a-b, with a range of $-9.0-15.2 \times 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$ in **ZnPc**-(R)/(S)/(rac) and $-6.2{-}10.6\times10^4~\text{deg}~\text{T}^{-1}~\text{m}^{-1}$ in CuPc- $(\mathbf{R})/(\mathbf{S})/(\mathbf{rac})$. This difference, even if treated as significant, was much smaller than that observed in previously mentioned polymeric systems.^{11,12} However, the observed Faraday rotation in the polymeric systems displaying a paramagnetic

enhancement was not consistent with the Faraday A-term line shape, and eq 3 does not include a term for the ground state magnetic moment of the chromophore. Ground state magnetic moments are instead expected to influence Faraday rotation in materials with resonance enhancement due to Faraday C-term mechanisms, which require degenerate electronic ground states. The π to π^* transitions which are responsible for the Q-band are confined to the phthalocyanine ligand, and do not posess degenerate electronic ground states. The absence of a large paramagnetic effect on the magneto-optical performance of the phthalocyanine chromophore is consistent with our assignment of the A-term mechanism as the dominant factor giving rise to Faraday rotation in phthalocyanine derivatives.

Phthalocyanine lanthanide complexes are also of interest for the study of Faraday rotation, as they incorporate highly polarizable metal centers containing high numbers of unpaired electrons. Some multidecker Pc structures have even been shown to act as single-molecule magnets,³³ presenting thermally activated magnetic relaxation with relatively high effective barriers. Similar features, namely, high polarizability, numerous unpaired spins, and magnetic ordering, are found in the highest performance inorganic garnets, such as TGG. With this in mind, the terbium double-decker phthalocyanine complex TbPc2-(rac) was targeted, and the recorded MCB spectrum is shown in Figure 5c. The 320 nm thick thin film of **TbPc**₂-(**rac**) achieved a maximum Verdet constant of $-7.3 \times$ $10^4 \text{ deg } \text{T}^{-1} \text{ m}^{-1}$ at 680 nm, with a line shape consistent with the Faraday A-term. This value is similar to other transition metal phthalocyanines reported in this work. Therefore, it can be concluded that proximity of a polarizable and spin-rich lanthanide ion does not greatly perturb the π -electron system

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of the phthalocyanine ligands, at least not in a manner which affects the resonance-enhanced Faraday rotation associated with the Q-band of phthalocyanines. As in **CuPc**, this result highlights the primacy of the π -electron system of the phthalocyanine ligand in determining the Faraday rotation of the material.

In contrast, increased substitution at the periphery of the phthalocyanine core in octathianthrene-substituted zinc phthalocyanine ZnPc-OT led to a Verdet constant of $-33 \times$ 10^4 deg T⁻¹ m⁻¹ at 800 nm, which is among the largest reported Verdet constants for an organic material. The observed line shape supports a Faraday A-term origin (Figure 5d). The pronounced redshift in the Q-band absorption is consistent with behavior observed in other phthalocyanines having substitution at the "inner" sites³⁴ and is thought to arise from sterically induced twisting of the chromophore's π electron system.³⁵ The figure-of-merit value of $-0.046 \text{ deg } \text{T}^{-1}$ was smaller in magnitude for ZnPc-OT than that for both ZnPc-(R) and ZnPc-(rac), indicating that optical absorption and magneto-optical activity increase simultaneously in this system. This observation is consistent with eq 3, in that, the magnitude of the Faraday A-term is proportional to the magnitude of the electric transition dipole moment. Thin films of ZnPc-OT formed microscopic cracks when subjected to thermal annealing, lowering their optical-quality and Verdet constant (Figures S3g and S4g). The combination of large magneto-optical activity, near-infrared absorption, good optical-quality thin films, and simple preparation make ZnPc-OT an attractive candidate for incorporation into magneto-optical devices wherein low optical density is not a requirement.

CONCLUSION

In summary, our investigation of 11 porphyrin, subphthalocyanine, and phthalocyanine derivatives demonstrates the rational tunability of the large magneto-optical response observed in a series of electronically similar chromophores. The key magneto-optical properties of these optical-quality thin films are summarized in Table 1. The spectral coverage of the species that were studied spans much of the visible and near-infrared regions, bookended by RuTPP and ZnPc-OT, which reached maximum absolute Verdet constants of $-24 \times$ $10^4 \text{ deg } \text{T}^{-1} \text{ m}^{-1} \text{ at 530 nm and } -33 \times 10^4 \text{ deg } \text{T}^{-1} \text{ m}^{-1} \text{ at 800}$ nm, respectively. Five other species in this study also achieved maximum absolute Verdet constants greater than $10^5 \text{ deg } \text{T}^{-1}$ m⁻¹, which is comparable to those of other high-performance thin-film Faraday rotator materials. The origin of the large magneto-optical response is attributed to Faraday A-term resonance enhancement associated with the degenerate electronic transitions that are responsible for the Q-band in porphyrins, subphthalocyanines, and phthalocyanines. Chemical modifications of the chromophore cores, like the addition of chiral side chains and the introduction of paramagnetic metal centers, were shown to have little effect on the magnitude of the maximum Verdet constant. However, both the introduction of different metal centers in tetraphenyl porphyrin derivatives and increased peripheral substitution in a phthalocyanine derivative made significant impacts on the magnitude of the Verdet constant. The maximum thin film thickness of 320 nm achieved here by TbPc2-(rac) was less than the 1 to 5 μ m typical for applications of MO thin films,^{3,4,36} such as those in magneto optical imaging. Efforts to fabricate thicker films using alternative techniques to spinpubs.acs.org/JACS

Table 1. Measured Verdet constants and Figures-of-Merit for Phthalocyanine, Subphthalocyanine, and Porphyrin Derivatives

Entry	Species	λ _{max} Faraday Rotation (nm)	Verdet Constant × 10^4 (deg T ⁻¹ m ⁻¹)	Figure of Merit ^a (deg T ⁻¹)
1	RuTPP	530	-24.2 ± 2.9	-0.05210 ± 0.0007
2	ZnTPP	560	-6.2 ± 0.7	-0.01915 ± 0.0006
3	CuPc- (S)	620	-10.6 ± 1.4	-0.05278 ± 0.0011
4	CuPc- (rac)	620	-6.2 ± 0.6	-0.03873 ± 0.0015
5	CuPc- (R)	630	-9.9 ± 1.1	-0.05316 ± 0.0012
6	ZnPc- (S)	640	-9.0 ± 0.9	-0.04785 ± 0.0012
7	ZnPc- (rac)	640	-14.1 ± 1.6	-0.06981 ± 0.0014
8	ZnPc- (R)	640	-15.2 ± 1.8	-0.06897 ± 0.0014
9	SubPc	650	-11.1 ± 0.7	-0.03497 ± 0.0004
10	TbPc ₂ - (rac)	680	-7.3 ± 1.2	-0.05520 ± 0.0030
11	ZnPc- OT	800	-33.1 ± 2.6	-0.04615 ± 0.0005

^aDefined as Faraday rotation divided by absorbance.

coating, such as hot-pressing or blade-coating, are ongoing. Given the massive structural diversity of phthalocyanines and porphyrins in the literature, there are abundant opportunities to create high-performance Faraday rotator materials from these structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c02113.

Experimental procedures, details of the characterization of the chromophores and synthetic intermediates, details of the Faraday rotation measurement and instrument, theoretical calculations, UV–vis, ¹H and ¹³C NMR, and MALDI mass spectra (PDF)

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Notes

The authors declare no competing financial interest.

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