DOI: 10.1002/anie.200802687

Porphyrin Dimer Carbocations with Strong Near Infrared Absorption and Third-Order Optical Nonlinearity**

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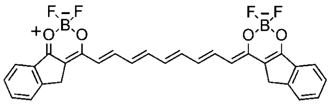
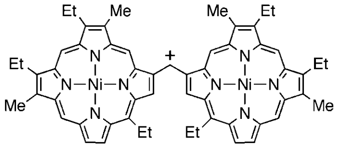
Materials with large ultrafast third-order nonlinearities at near-infrared (NIR) wavelengths are required for all-optical signal processing.[1] Telecommunications systems operate in this spectral region, and all-optical switching[2] and wavelength conversion[3] devices will lead to faster signal processing than can be achieved by current electronic methods, thus providing greater bandwidths and data-transfer rates. Dyes with large optical nonlinearities will be used in a new generation of devices requiring modest drive powers and short path lengths,[4] and in ultrafast image-correlation security systems.[5]

Herein we present a family of porphyrin dimer carbocations **1a–c** which show intense NIR absorption maxima at 1100–1340 nm and large ultrafast third-order nonlinearities at 1550 nm. It is well known that carbocations tend to be more electronically delocalized than neutral conjugated hydrocarbons, and many common dyes, such as cyanines and rhodamines, can be regarded as resonance-stabilized carbocations. Cyanines are interesting in that they have large negative third-order nonlinearities at energies below the S_0–S_1 gap.[6,7] Furthermore, the optical nonlinearity of cyanine dyes scales with a high-order power of the conjugation length, suggesting that extended cyanines could provide extremely large nonlinearities.[7] However, extended cyanines can undergo a symmetry-breaking process which reduces electronic delocalization and nonlinearity.[8] Hales et al. recently reported that extended bis-(dioxaborine) polymethine **2** sustains delocalization at lengths of approximately 14 conjugated bonds, beyond that of conventional cyanines.[9] The nature of the terminal groups evidently plays a key role in achieving efficient electronic delocalization in long chromophores. The idea behind this work is to synthesize a cyanine-like dye with two-dimensionally delocalized porphyrin macrocycles as terminals (Figure 1), thus accessing greater effective delocalization lengths. The conjugated bridge of our "porphocyanines" differs from those in standard cyanine dyes in that we utilize triple rather than double bonds; alkynes provide better electronic coupling to porphyrins because they cannot twist out of conjugation.[10]



2 (λ_{max} 926 nm)



3 (λ_{max} 1030 nm)

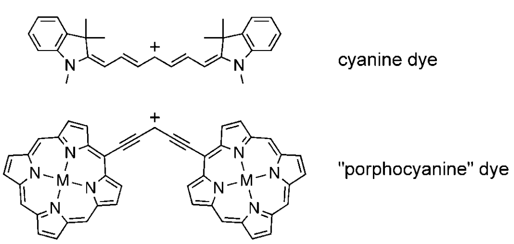


Figure 1. The concept of porphyrin dimer carbocations as cyanine dye analogues.

Neutral conjugated porphyrin oligomers[11] and polymers[12] have been shown to exhibit large third-order optical nonlinearities. Porphyrin-stabilized carbocations have scarcely been investigated,[13] although Smith and co-workers reported formation of cationic porphyrin dimer **3** with NIR absorption ($\lambda_{max} = 1030$ nm; $\varepsilon = 41\,500\,\mathrm{M^{-1}\,cm^{-1}}$),[14] indicating significant charge delocalization.

Porphocyanine **1a** was synthesized as shown in Scheme 1. Deprotonation of the terminal acetylene **4** and reaction with 0.5 equivalents of methyl benzoate afforded the precursor **5a** in 50% yield. Addition of trifluoracetic acid (TFA, 2% by volume) to **5a** generated carbocation **1a**, as revealed by dramatic changes in the UV/Vis/NIR spectrum (**1a**: $\lambda_{max} = 1243$ nm; $\varepsilon = 170\,000\,\mathrm{M^{-1}\,cm^{-1}}$) and by NMR spectroscopy. The NIR bands are substantially red-shifted in comparison to neutral porphyrin oligomers. In addition, the absorption is even red-shifted in comparison to the previously reported β-linked dimer **3**, as a result of the more efficient conjugation

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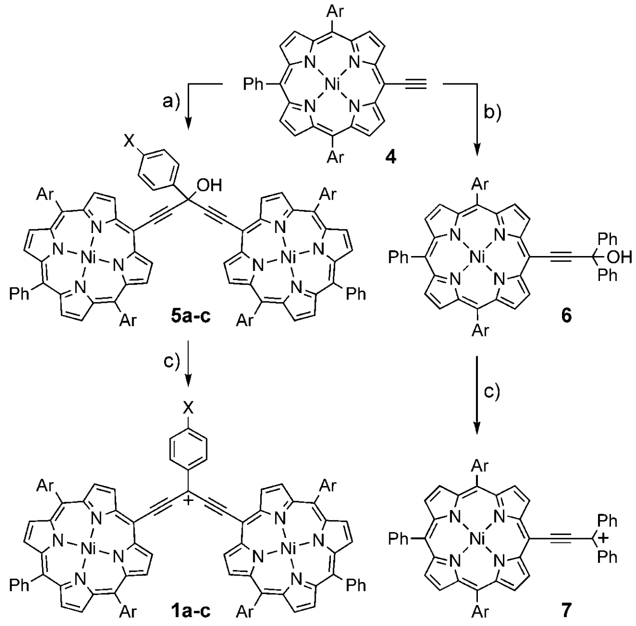
[**] This work was supported in part by the STC Program of the National Science Foundation under Agreement Number DMR-0120967 and the DARPA MORPH Program and ONR (N00014-06-1-1013 and N00014-06-1-0897). We thank Prof. S. R. Marder and Dr. S. Barlow for valuable discussion and the EPSRC Mass Spectrometry Service (Swansea) for mass spectra.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802687.



Scheme 1. Synthesis of cations **1a** (X=H), **1b** (X=NO_2), **1c** (X=OMe) and **7**. Ar=3,5-(tBu)$_2C_6H_3$. a) $XC_6H_4CO_2Me$ (0.5 equiv); $LiN(SiMe_3)_2$ (4 equiv), THF; b) Ph_2CO (1.5 equiv), $LiN(SiMe_3)_2$ (4 equiv), THF; c) F_3CCO_2H (TFA, 2% by vol.), $CHCl_3$.

through the *meso* positions. Cation formation is reversible; washing with water regenerates alcohol **5a** in 92% yield, as shown by absorption spectroscopy.

The wavelength of the NIR absorption band of **1a** can be tuned by placing electron-donating or electron-withdrawing substituents on the central phenyl ring to stabilize or destabilize the carbocation and thus to control the degree of delocalization onto the porphyrins. Thus a *para*-nitro substituent shifts the absorption to longer wavelength (Figure 2a. **1b**: $\lambda_{max} = 1348$ nm; $\varepsilon = 120000\,\text{M}^{-1}\text{cm}^{-1}$) whereas a *para*-methoxy substituent shifts it to shorter wavelength (**1c**: $\lambda_{max} = 1176$ nm; $\varepsilon = 110000\,\text{M}^{-1}\text{cm}^{-1}$).

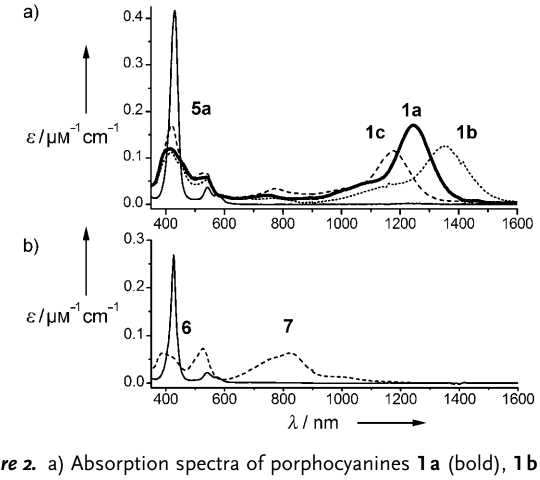


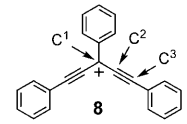
Figure 2. a) Absorption spectra of porphocyanines **1a** (bold), **1b** (dotted) and **1c** (dashed) in $CHCl_3$/2% TFA, in comparison with precursor alcohol **5a** (plain) in $CHCl_3$. Alcohols **5b** and **5c** gave essentially the same absorption spectra as **5a**. b) Absorption spectrum of porphyrin monomer carbocation **7** (dashed) in $CHCl_3$/2% TFA, and its precursor alcohol **6** (plain) in $CHCl_3$.

A reference compound (**6**), containing just one porphyrin, was synthesized by reaction of acetylene porphyrin **4** with benzophenone (Scheme 1). Upon formation of cation **7** by addition of TFA, a significant shift in the absorption spectrum was again observed (Figure 2b. **7**: $\lambda_{max} = 824$ nm; $\varepsilon = 62000\,\text{M}^{-1}\text{cm}^{-1}$). As the NIR band for porphocyanine dimer **1a** is red-shifted by over 400 nm ($\Delta E \approx 0.50$ eV) in comparison with monomer carbocation **7**, the positive charge must be delocalized over both porphyrin units in **1a**.

The linear optical properties of the porphocyanines show similarities with highly delocalized cyanine-like structures. The full widths at half maxima (FWHM) for the NIR bands are small: 920 cm^{-1} for **1a** compared to 1640 cm^{-1} for the Soret band of **5a**, indicating a small geometry change upon excitation. The large extinction coefficients of the NIR bands also indicate fully allowed transitions, as in standard cyanine dyes.

^{13}C NMR spectroscopy provides a direct probe for charge-delocalization in porphocyanine **1a**.[15] The most informative resonances are those of the quaternary carbons near the center of the molecule. These signals are difficult to assign by C–H correlation experiments, so it proved necessary to synthesize ^{13}C-labeled variants of compounds **5a** and **6** (from $Ph^{13}CO_2Me$ and $Ph_2{}^{13}CO$ respectively). The central carbon atom C^1 in the resulting porphyrin-stabilized cations **1a** and **7** carry less positive charge than C^1 in the corresponding aryl-stabilized cations **8** and **9**[16] (Table 1), as revealed by an upfield shift of 20–30 ppm in its chemical shift, δ_{C^1}. The chemical shift difference, between the C^1 atom of dimer **1a** and that of its reference monomer **7** is 27 ppm, confirming that the second porphyrin increases the delocalization of the positive charge.

Table 1: Selected ^{13}C NMR spectroscopic shifts (δ_C) and changes in chemical shift on cation formation from alcohol precursors ($\Delta\delta_C$) of porphyrin cations **1a** and **7**, measured at 298 K in $CDCl_3$/2% d-TFA, in comparison to phenyl stabilized analogues **8** and **9**.[16]



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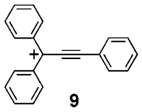

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	δ_{C1} ($\Delta\delta_{C1}$)	δ_{C2} ($\Delta\delta_{C2}$)	δ_{C3} ($\Delta\delta_{C3}$)
1a	133.9 (66.3)	118.9 (22.8)	136.1 (49.5)
7	160.8 (85.0)	113.0 (14.3)	163.6 (75.4)
8	162.1 (96.4)	106.5 (17.4)	145.5 (60.6)
9	186.6 (112.1)	105.9 (14.4)	159.1 (72.5)

The molecular third-order polarizability, γ, of carbocation **1a** and its alcohol precursor **5a** were determined by femtosecond-pulsed Z-scan measurements at 1550 nm. Representative results for both the open-aperture (sensitive to Im(γ)) and closed-aperture experiments (sensitive to Re(γ)) are shown in Figure 3 (Im(γ) and Re(γ) are the imaginary and real components of the molecular third-order polarizability). Despite the nearly five-fold decrease in irradiance, the magnitudes of the signals (proportional to the nonlinearity) for the carbocation solution dwarf those of the precursor. By

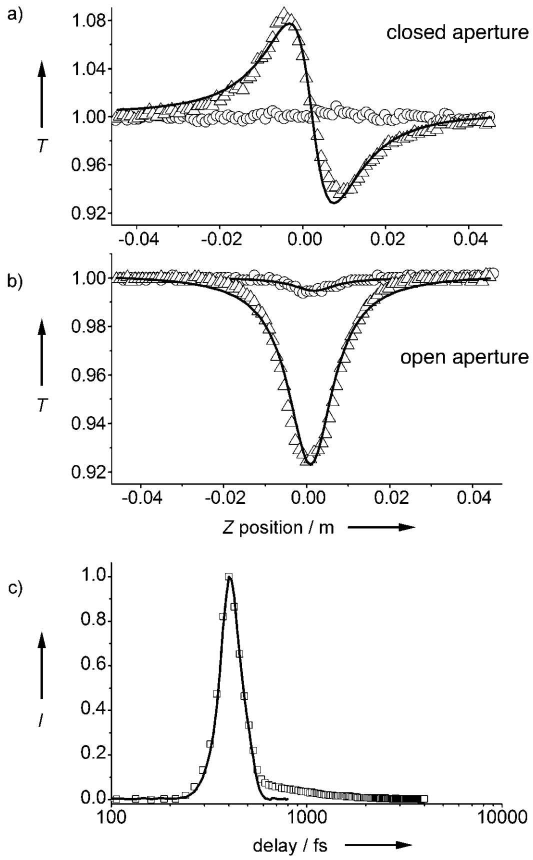

Figure 3. Closed- (a) and open-aperture (b) *Z* scans performed at 1550 nm for **1a** in $CHCl_3$/2% TFA (△) and **5a** in $CHCl_3$ (○) with 33 GW cm^{-2} and 148 GW cm^{-2} excitation irradiances respectively (50 Hz repetition rate). Solid lines are theoretical curve fittings described in the Supporting Information. Normalized TR-DFWM signal (c) at 1550 nm for **1a** in $CHCl_3$/2% TFA (□). The solid line shows the temporal response for a 500 μm slab of fused silica and reveals TR-DFWM instrument response.

fitting the *Z*-scan data for the solution of **1a**, assuming a purely third-order nonlinearity, the values for Re(γ) and Im(γ) were found to be -20.0×10^{-32} esu and 4.5×10^{-32} esu, respectively, compared to -5.3×10^{-32} esu and 1.2×10^{-32} esu for bis-(dioxaborine) polymethine **2**. One prominent feature is the extremely large negative value of Re(γ) at this wavelength. The extent of delocalization can be gauged by a comparison of the nonlinearity and position of the absorption maxima with other extended cyanine-like systems. These comparisons (see Supporting Information) point to a similar degree of delocalization but over a greater length of approximately 18 conjugated bonds for the bis-(porphyrin) cation **1a** compared to approximately 14 conjugated bonds for the bis-(dioxaborine) polymethine **2**. Another significant feature of **1a** is the large ratio of Re(γ)/Im(γ) (ca. 4.5) which indicates that the incident photon energy is detuned from two-photon absorption (2PA) resonances. Finally, the time-resolved degenerate four-wave mixing signal (TR-DFWM) for **1a** (Figure 3c) shows that the majority of the temporal response is pulsewidth-limited (<100 fs), with a small, slightly slower component ($\tau\approx700$ fs).

The uniqueness of cation **1a** lies both in the large ratio of Re(γ)/Im(γ), suggesting that an acceptable 2PA figure of merit (FOM)[17] could be achieved with this material, and in the magnitudes for each component of γ, which represent some of the largest off-resonant nonlinearities reported in this spectral region.[18] These attributes, coupled with the ultrafast response of the nonlinearity, imply that this system has the critical characteristics for all-optical switching. Furthermore, despite this large ratio, Im(γ) is also quite sizeable; it corresponds to a 2PA cross-section of ca. 3100 GM (at 1550 nm), which is even larger (on a per-macrocycle-basis) than those of conjugated porphyrin polymers with sizable values in this spectral region.[19,20]

In summary, a porphyrin dimer carbocation has been synthesized and was found to have effective delocalization over approximately 18 conjugated bonds, significantly longer than traditional cyanine dyes. The resulting large third-order nonlinearities at 1550 nm and two-photon absorption figure of merit suggest that these dyes are promising materials for all-optical switching and dynamic noise suppression.

Received: June 7, 2008

Keywords: carbocations · dyes/pigments · materials science · nonlinear optics · porphyrinoids

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