Supporting Information
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Application of Near-IR Absorption Porphyrin Dyes Derived from Click Chemistry as Third-Order Nonlinear Optical Materials

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Supporting Information

1. Experimental

Reagents were purchased from commercial sources (Aldrich) and used without further purification. Triethylamine (TEA) and tetrahydrofuran (THF) were distilled and purged with argon before use. TCNE and TCNQ were purchased from Aldrich and all other reagents were purchased from commercial sources and used as received.

$^1$H-NMR spectra of the samples were recorded with a Varian 400 MHz instrument in CDCl$_3$ using the residual solvent resonance of CHCl$_3$ at 7.26 ppm relative to SiMe$_4$ as internal reference. Fourier transform infrared spectra (IR) were recorded in KBr pellets using a Perkin Elmer LR-64912C spectrophotometer. MALDI-TOF-MS spectra were determined on a Shimadzu AXIMA-CFR mass spectrometer. All UV-visible spectra were recorded on a HITACHI U-3010 spectrophotometer. Scanning electron microscopic (SEM) images were obtained on a Jeol JSM-5400/LV with accelerating voltage of 15 kV.

2. Z-scan measurement

The nonlinear optical properties (NLO) response of the compounds were measured by means of
Z-scan technique, employing 21 ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser (EKSPLA PL2143B). The linearly polarized laser beam was focused with a 200 mm focal length lens and the sample was moved across the focus by means of a computer controlled micrometric translation stage. The pulse energy, after suitable attenuation, was in the range 0.3–0.9 μJ. Z-scan is a relatively simple experimental technique allowing for the simultaneous determination of the real and imaginary parts of the third-order susceptibility $\chi^{(3)}$. [1] All of the samples were measured at $10^{-6}$ M solution in THF (specpure) and the solvent itself does not show any third-order nonlinearity under our experimental conditions. [2]

The details of the experimental techniques, as well as the procedure to analyze the experimental data, will be briefly described here, as extended information can be found in the literature. Here a laser beam is focused using a lens and passed through the sample. The beam’s propagation direction is taken as the z-axis, and the focal point is taken as $Z = 0$. The beam will have maximum energy density at the focus, which will symmetrically reduce toward either side for the positive and negative values of $Z$. In our experiment, THF solutions of the samples were taken in 1 mm cuvettes and the measurement was done by placing the samples in the beam at different positions with respect to the focus (different values of $Z$) and measuring the corresponding light transmission. The graph plotted between the samples $T_{\text{norm}}$ (transmission normalized to the linear transmission of the sample) was known as the Z-scan curve. From the “open aperture” Z-scan curves the nonlinear absorption coefficient ($\beta$) has been determined using the equation

$$\beta (m \cdot w^{-1}) = \frac{2\sqrt{2} \left[ 1 - T(Z = 0) \right]}{I_0 L_{\text{eff}} (1)}$$

where $T$ is the normalized transmittance, $L_{\text{eff}} = (1 - \exp \left(-\alpha_0 L_0\right)) / \alpha_0$ is the effective thickness.
of the sample, \( \alpha_0 \) is the linear absorption coefficient of the sample at the laser excitation wavelength, \( L \) is the sample thickness, and \( I_0 \) is the on-axis irradiance at the focus. From the nonlinear absorption coefficient the imaginary part of the third-order nonlinear susceptibility has been determined using the equation

\[
\text{Im}\chi^{(3)}(\text{esu}) = \frac{c^2 n_0^2 \beta}{240 \pi^2 \omega} \tag{2}
\]

where \( c \) is the speed of light in m \( \cdot \) s\(^{-1} \), \( n_0 \) is the linear refractive index, and \( \omega = \frac{2\pi c}{\lambda} \) is the fundamental frequency in cycles \( s^{-1} \).

From the “closed aperture” Z-scan curves the nonlinear refraction coefficient \( (n_2) \) has been determined using the equation

\[
n_2(m \cdot w^{-1}) = \frac{\Delta T_{pv}}{0.406(1 - s)^{0.75}kL_{\text{eff}}} \tag{3}
\]

Where \( \Delta T_{pv} = T_{\text{peak}} - T_{\text{valley}} \), and \( k = \frac{2\pi}{\lambda} \) is the wave vector. The real part of the third-order nonlinear susceptibility has been determined using the equation

\[
\text{Re}\chi^{(3)}(\text{esu}) = \frac{n_0^2 c n_2}{120\pi^2} \tag{4}
\]

The \( \chi^{(3)} \) can be calculated by Eq.(5)

\[
|\chi^{(3)}| = \sqrt{|\text{Im}\chi^{(3)}|^2 + |\text{Re}\chi^{(3)}|^2} \tag{5}
\]

3. Solvent-exchange self-assembly method

Self-assembly of these porphyrin derivatives were conducted by using the solvent-exchange method in the solution phase, which transfers the molecules from a good solvent (CH\(_2\)Cl\(_2\)) into a poor solvent (methanol) where the molecules have limited solubility, and thus self-assembly occurs through weak interactions such as \( \pi-\pi \) stacking and hydrogen bonding. This approach takes the advantage of the strong intermolecular \( \pi-\pi \) interactions, which are enhanced in a poor solvent where the molecules have minimum interaction with the solvent. Similar methods have previously
been used for self-assembling microstructures of π-conjugated organic molecules. [3-5] In our experiments, we used a solution-injection method to facilitate the self-assembly in the methanol medium. Typically, a minimum volume (50 μl) of a concentrated CH₂Cl₂ solution (0.001 M) of sample was injected rapidly into a larger volume (5 ml) of methanol, followed by immediate mixing. Thus, the mixed solution contained only a slight amount of CH₂Cl₂, resulting in the effective self-assembly of the molecule. Such a solvent provided limited solubility for compounds, but on the other hand led to favorable molecular π-π stacking.

Reference

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