Water-soluble Self-assembled Butadiyne-bridged Bisporphyrin: a Potential Two-Photon Absorbing Photosensitizer for Photodynamic Therapy

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2PA calculations.

References:

The curve fits were performed according to the theoretical expression for the transmittance.

\[
T(\zeta) = \frac{(1 - R)^2 e^{-(\alpha(1)L)}}{\sqrt{q(\zeta)} \int_{-\infty}^{\infty} \ln[1 + q(\zeta) e^{-(z^2)}}] \, dx
\]

(1)

\[
q(\zeta) = \frac{q_0}{1 + \zeta^2}
\]

(2)

\[
q_0 = \alpha(2) (1-R) I_0 L_{\text{eff}}
\]

(3)

\[
L_{\text{eff}} = \frac{1 - \exp(-\alpha(1)L)}{\alpha(1)}
\]

(4)

\[
\sigma(2) = \frac{h \omega \alpha(2)}{N}
\]

(5)

where \(\zeta\) is the normalized \(z\)-position \((\zeta = (z-z_0)/z_R)\), and \(z_0\) and \(z_R\) are the focal position and the Rayleigh range, respectively. \(q_0\) is the two-photon absorbance, \(\alpha(1)\) is the one-photon absorption coefficient, \(R\) denotes the Fresnel reflectance, and \(L\) is the path length (1 mm). \(\alpha(2)\) is the 2PA coefficient, \(L_{\text{eff}}\) denotes the effective path length, and \(I_0\) is the peak intensity at the focal position. \(N\) is the number density of the solute molecules and \(h \omega\) is the photon energy of the incident light. Finally, the effective \(\sigma(2)\) value was estimated from equation (5).
(SI) Fig 1. Expanded $^1$H-NMR spectrum of 7 in CDCl$_3$ at r.t., 600 MHz.
(SI) Fig. 2. HHCOSY spectrum of 7 in CDCl$_3$ at rt, 600 MHz.

( SI) Fig. 3. Excitation Spectrum of 7 in CHCl$_3$ monitored at 737 nm.

( SI) Fig. 4. Preparative GPC spectrum of (5Zn)$_2$ and 6$_n$ (n=1,2,3…), reorganized from a 2:1 mixture of 5Zn:3Zn. (JAIGEL 3H; 2 columns connected in series, eluent: CHCl$_3$, flow rate: 3.5 mL/min) Only the tetramer fraction 6$_1$ (shaded area) was collected for metathesis reaction in order to recycle the starting materials.
(SI) Fig. 5. Analytical GPC spectrum of 7 (JAIGEL 3H-A; eluent: CHCl₃) monitored at 480, 420, 350 and 300 nm (top to bottom).

(SI) Fig. 6. Analytical GPC spectrum of 7 (Tosoh TSKgel G2500HHR; eluent: pyridine) monitored at 420 and 350 nm (upper and lower left), and 480 and 300 nm (upper and lower right).
(SI) Fig. 7. MALDI-TOF mass spectrum of 1 shows the target peak at \( m/z = 3780.9 \) (\( M+H^+ \)), calculated for 7H \( C_{198}H_{194}N_{28}O_{36}Zn_4 \) 3779.36.

(SI) Fig. 8. UV-vis absorption spectra of 0.215 mM of 1 in water (broken line) and 0.196 mM of 1 in water in the presence of excess pyridine (solid line).