Supporting Information

Octupolar Bis(porphyrinato) Terbium(III) Complex with the Highest Off-resonant Hyperpolarizability

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Computational Details

Geometry optimization. For an empirical dispersion-corrected density functional theory (DFT-D), Grimme's scheme was adopted, where the van der Waals interaction term is well described by a damped interatomic potential, accounting for long-range dispersion effects in noncovalent systems.[1] The total density functional energy $E_{DFT\text{-}D}$ can be written as $E_{DFT-D} = E_{DFT} + E_D$, where E_{DFT} is the normal self-consistent density functional energy, and E_D is the empirical dispersion correction term. E_D is calculated by $E_D = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \dfrac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij})$, where s_6 is a global scaling factor only depending on the applied density functional method, C_6^{ij} is the combined dispersion coefficient for atom pair i and j, R_{ij} is the distance between atoms i and j, N is the number of atoms, and $f_{dmp}(R_{ij})$ is the damping function, which is expressed by

$f_{dmp}(R_{ij}) = \dfrac{1}{1 + e^{-20\left(\frac{R}{R_0} - 1\right)}}$. As the basis set is concerned, Pople basis sets are proved excellent for calculating the structure and properties of porphyrins, phthalocyanines, fullerenes, and their analogues, leading to many applications in this field.[2] In addition, the Stuttgart RSC Segment/ECP basis set shows good performance for transition metal atoms.[3] As a consequence, a frequently-used DFT-D functional, ωB97XD, is employed for geometry optimization in the present work. The basis set of 6-311+G(d) and MWB28 is chosen for C/H/N/O and Tb, respectively.

Noncovalent interaction. In order to clarify the π-π interactions, the noncovalent interaction calculation is carried out using the reduced density gradient (RDG) theory, which is

calculated by $S_{RDG} = \dfrac{1}{2(3\pi^2)^{1/3}} \dfrac{|\nabla\rho|}{\rho^{4/3}}$, where ρ is the electron density of the whole system. The

interaction type is identified as $\Omega = Sign(\lambda_2)\rho$, where $Sign(\lambda_2)$ is the sign of the second largest

eigenvalue of electron density Hessian matrix. According to Johnson and Yang's theory, $\Omega <$ -

0.01, $\Omega > 0.01$, and -0.01 $< \Omega < 0.01$ indicate attractive interaction (such as dipole-dipole or

hydrogen bonding), nonbonding interaction, and van der Waals interaction, respectively.[4] The

reduced density gradient map is plotted using VMD 1.8.7[5] with the isovalue of 0.60 a.u.

Validity of the present calculating level ωB97XD/6-311+G(d)/MWB28

Validity of present mixed basis set. As far as the electronic structures of organometallic

systems are concerned, a type of mixed basis set obtained by combination of triple-zeta Stuttgart

RSC Segment/ECP basis set (RECP)[6] for lanthanide and triple-zeta split-valence Pople basis sets

for short-period elements was proved as an more accurate description than the mixture of double-

zeta LanL2DZ for lanthanide and double-zeta split-valence Pople basis sets for short-period

elements.[7]

Validity of DFT-D in the field of π-π interaction. For more than a decade, it has been

known that common density functional theory (DFT) cannot describe the long-range dispersion

interaction correctly,[8] because DFT does not provide the $-\dfrac{C_6}{R^6}$ dependence of the dispersion

interaction energy on the intermolecular distance R originated from the induced dipole

moments.[9] Grimme and co-workers developed a brief description of this $-\dfrac{C_6}{R^6}$ behavior of long-

range interaction named as DFT-D, which has been repeatedly proved successful for the noncovalent interaction calculation.[10]

The reason we choose ωB97XD. As the supramolecular systems with obvious π-π interaction are concerned, MP2 always overestimates the interaction energy.[11] In addition, the calculation of SCS-MP2, M05/06, or even CCSD(T) is nearly impossible for such a big system including 3580 basis functions and 6287 primitive gaussians. Among various DFT-D theories, ωB97XD has been proved stable and accurate for many noncovalent interaction systems without unacceptable computational amount.[12]

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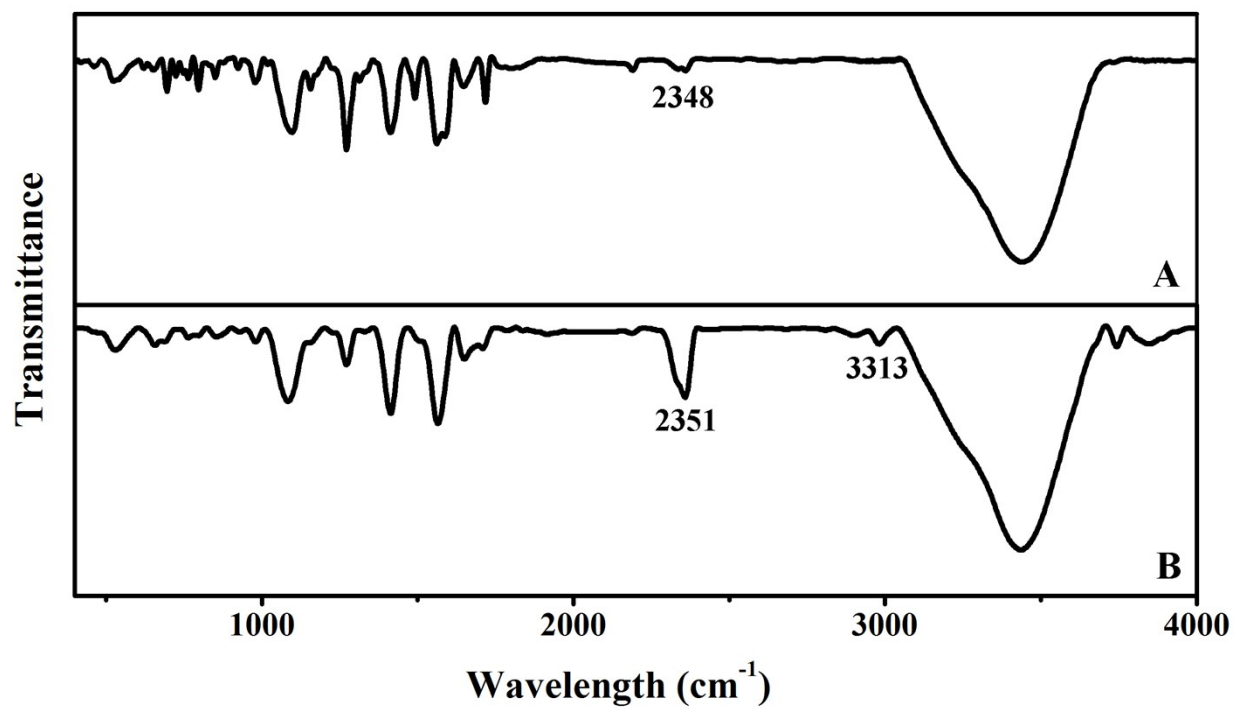
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HTb(DADAPor)$_2$

Mol Weight
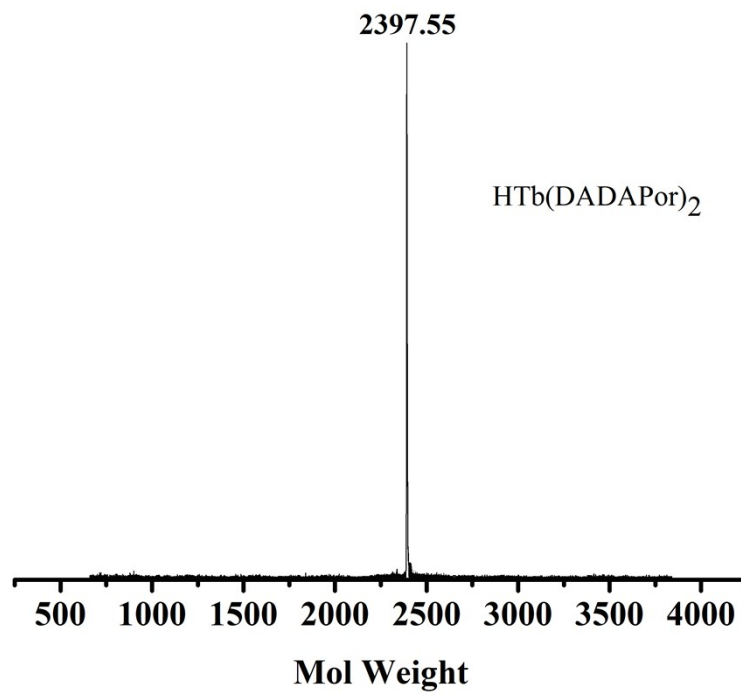
Figure S1. Mass Spectrum of HTb(DADAPor)$_2$.
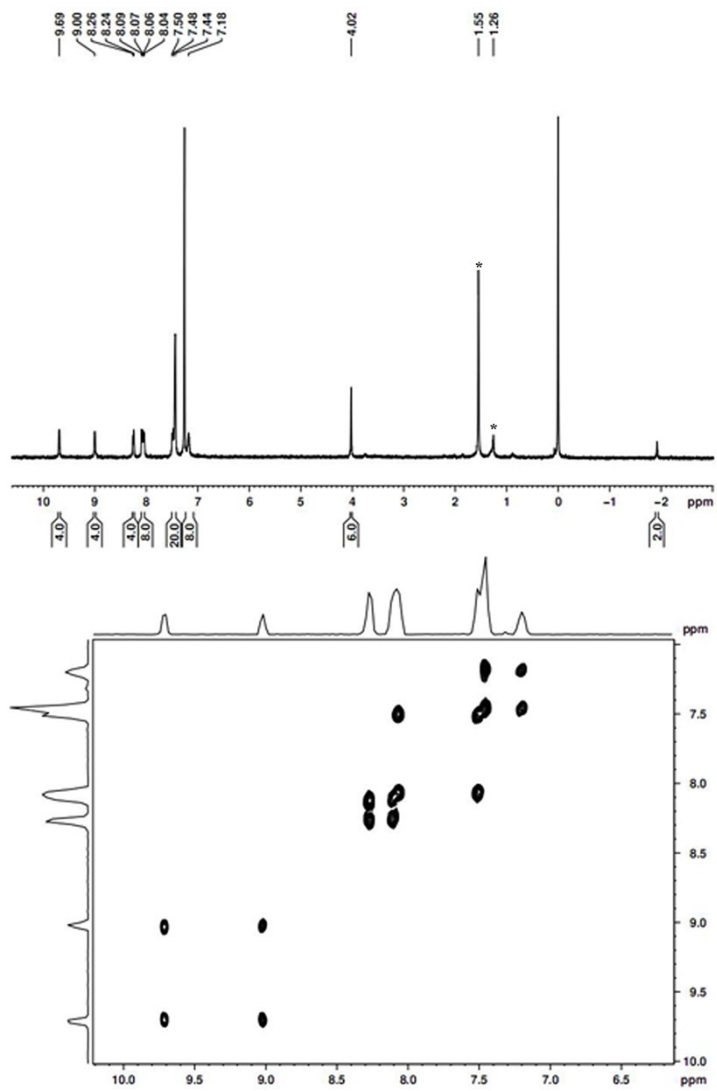
Figure S2. Mass Spectrum of HTb(DADAPor)₂.

Figure S3. The IR spectra of $H_2DADAPor$ and $HTb(DADAPor)_2$.

Table S1. Mass spectroscopic and elemental analysis data for $H_2DADAPor$ and $HTb(DADAPor)_2$.

Compound	Molecular Formula	Yield (%)	M$^+$ (m/z)[b]	Analysis (%)[a(b)]		
				C	H	N
Metal free porphyrin	$C_{76}H_{52}O_4N_6$ [c]	67%	1116.63 (1115.54)	81.58 (81.99)	4.92 (4.71)	7.91 (7.55)
Double-decker	$C_{152}H_{100}O_8N_{12}TbH$ [d]	25%	2397.55 (2397.41)	76.84 (76.66)	4.62 (4.23)	7.25 (7.06)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the protonated molecular ion M$^+$. [c] Contain 1.0 equiv. of solvated CH_3OH and 1.0 equiv. of H_2O. [d] Contain 1.0 equiv. of solvated H_2O.

Table S2. Electronic absorption and fluorescence spectra data for $H_2DADAPor$ and $HTb(DADAPor)_2$ at the concentration of 2.0×10^{-6} M in $CHCl_3$.

Compound	λ_{abs} / nm (in $CHCl_3$)			λ_{em}/ nm (in $CHCl_3$)
Metal free porphyrin	443	607	698	712
Double-decker	445	660	—	649