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An octupolar bis(porphyrinato) terbium(III) complex with the highest off-resonant hyperpolarizability†

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A novel bis(porphyrinato) terbium double-decker complex HTb(DADAPor)$_2$ with a twisted cuboid octupolar molecular symmetry exhibits the largest off-resonant first hyperpolarizability, as evaluated by harmonic light scattering measurements with $\sqrt{(\beta_{HLS}{}^2)}_{1907} = 1700 \times 10^{-30}$ esu.

Octupolar molecules with highly delocalized π-electron systems have paved new ways in the development of new nonlinear optical (NLO) molecular materials due to their broader range of nonlinear tensorial coefficients in comparison with the more common dipolar one-dimensional D–π–A schemes.[1,2] The most general 3D octupolar architecture is made of a cube bearing eight alternatively positive and negative charges at its corners (that are induced by the presence of electron-donors and electron-acceptors) and strong electronic interactions between donor and acceptor groups along the cube edges.[3] In addition, this "perfect" octupolar cubic geometry displays an overall tetrahedral symmetry (T_d). However, practical octupolar molecular NLO materials developed up to date usually take reduced dimensionality.[3c] For example, projecting the charges of the octupolar cube on a plane perpendicular to the three-fold symmetry axis of the cube and containing its center result in a 2D alternate distribution of three negative and three positive charges.[1a] In fact, 3D octupolar molecules with a cube conformation and/or a tetrahedral symmetry are still remaining extremely rare[4] since strong NLO responses require highly conjugated electronic distributions corresponding to a planar molecular geometries. However, new species of octupolar NLO rare earth complexes composed of a ABAB-type phthalocyanine ligand associating two kinds of alternative substituents with slightly different electron-donating properties at the peripheral positions were recently developed.[5] These compounds take advantage of an intense intramolecular π–π interaction

between the two phthalocyanines in a bis(phthalocyaninato) rare earth(III) sandwich complex.

Porphyrins, as another important class of tetrapyrrole system with a large polarizable π-conjugated system, have also been extensively involved in the design and synthesis of typical NLO molecular materials because of their large oscillator strengths and substantial polarizabilities.[6] In particular, the porphyrin-based D–π–A systems mediated by an ethynyl unit between porphyrin and other strong oscillators usually create unusually polarizable and hyperpolarizable structures, and therefore enable the development of a variety of materials that possess unusual NLO properties.[7] However, all porphyrin-based 3D molecules developed so far are in fact assemblies of a few (3 or 4) porphyrin units organized in a tetrahedral geometry by binding them together to a single sp³-hybridized atom (carbon, silicon) that prevents from any significant electronic interactions between porphyrin moieties.[8] Truly porphyrin-based octupolar molecules employing the cubic molecular structure with eight alternating charges at the cube corners with noticeable electronic interactions between electron donor and electron acceptor groups has not yet been reported.
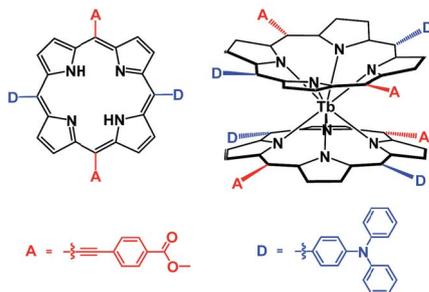
In the present paper, a metal free porphyrin featuring a crosswise DADA arrangement for the electron-donating and electron-withdrawing groups at the four *meso*-positions, namely 21H,23H-[5,15-bis(4-carboxyethyl-ethynyl)-10,20-bis(4-diphenyl-amino)phenyl]porphyrin, was designed and synthesized. The bis(porphyrinato) terbium double-decker complex HTb(DADAPor)$_2$ fabricated from this novel porphyrin ligand affords a typical generic template of an octupolar molecule with a relatively lower symmetry, D_2, than the T_d symmetry displayed by a truely octupolar cube, Scheme 1. This symmetry, in combination with an intense intramolecular π–π interaction and the lack of any absorption beyond 800 nm due to the reduced protonated nature of the double-decker molecule, is expected to result in a high off-resonant first hyperpolarizability for this double-decker compound.[3–5]

Special attention will be paid here to the contribution of resonance effects to the first hyperpolarizability β. Oudar and

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Scheme 1 Schematic molecular structures of the DADA-type metal free porphyrin H_2(DADAPor) and double-decker HTb(DADAPor)$_2$.

co-worker have proposed a two-level dispersion model to account for the resonance effects in the destination of β values.[2] If the fundamental laser frequency is close to the resonance frequency (ω_0)] or its first harmonic $(2\omega_0)$, in which 0 corresponds to one of the absorption bands of the molecule, the NLO property[9] can be strongly increased due to the significant resonance contribution. According to the very recent theoretical study, the resonant hyperpolarizability for bis(phthalocyaninato) yttrium skeleton becomes 10 to 10^3 times larger than the off-resonant value.[10] As a consequence, a off-resonant hyperpolarizability $\beta(0)$ should be taken as the evaluating criterion to compare the intrinsic NLO activities among various molecular materials.

It has been revealed that the electronic polarizability and the nature of the transitions between electronic states for molecular materials are responsible for the NLO response. As a consequence, for the purpose of engineering NLO chromophores, careful consideration over the molecular symmetry must be taken into account. Noncentrosymmetry being a necessary prerequisite for all even-order nonlinear effects, the donor–bridge–acceptor (D–Br–A) moiety has been developed as a typical classic molecular architecture for the dipolar moment molecule. Associated with their large π-conjugated systems, a number of porphyrin-bridged dipolar D–π–A chromophores featuring large dynamic hyperpolarizabilities have been developed.[11] However, the ground-state electrostatic interaction for dipolar molecules usually favors a detrimental centrosymmetric aggregation in the condensed phase, which in turn minimizes the second-order NLO properties. Aiming to overcome this drawback in the case of dipolar D–porphyrin–A chromophores, porphyrin-based octupolar compounds were proposed as alternative molecules. With the robust and benchmark dipolar chromophore, ruthenium(II)[5-(4′-ethynyl-(2,2′;6′,2″-terpyridinyl))-10,20-bis(2′,6′-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)-(2,2′;6′,2″-terpyridine)$^{2+}$ bis-hexafluorophosphate(RuPZn) as starting material, a porphyrin-containing supramolecular system displaying an octupolar NLO response was created.[12] Nevertheless, taking advantage of the intense intramolecular π–π interaction in bis(phthalocyaninato) rare earth(III) complexes, new species of octupolar NLO molecular materials composed of the most important artificial porphyrin analogue, phthalocyanine, with ABAB-type arrangement bringing two kinds of alternative substituents with slightly different electron-donating ability at the peripheral positions, were also developed.[5] However, the absorption band between 800–1100 nm

for bis(phthalocyaninato) lutetium compound [Lu(Pc*)$_2$] associated with the presence of one unpaired electron in the double-decker molecule is responsible for a strong absorption of the scattered light at the second harmonic wavelength (953 nm) by the chromophore,[13] indicating a significant contribution of multilevel resonance enhancements to the second-order NLO response of Lu(Pc*)$_2$.

In the present case, in order to construct the target octupolar bis(porphyrinato) terbium double-decker complex, a novel DADA-type metal free porphyrin has been synthesized. In order to strengthen the electron-donor and electron acceptor character of D and A, respectively, two carboxymethyl-phenylethynyl substituents as typical electron-accepting groups were introduced onto the opposite *meso*-positions of the porphyrin ligand while two di(phenylamino)phenyl moieties as typical electron-donating groups were grafted onto the remaining two opposite *meso*-positions. As a result, the metal free [5,15-bis(4-carboxymethyl-phenylethynyl)-10,20-bis(4-diphenylamino) phenyl] porphyrin H_2(DADAPor) was designed and synthesized for the first time, (Scheme 1). Its reaction with Tb(acac)$_3 \cdot n$H$_2$O (acac = acetylacetonate) in refluxing 1,2,4-trichlorobenzene (TCB) led to the first bis(porphyrinato) terbium(III) double-decker complex HTb(DADAPor)$_2$ exhibiting a typical generic template of a 3D octupolar molecule with a D_2 symmetry, Scheme 1. In particular, the reduced protonated nature of this double-decker species excludes any absorption in the near-IR range beyond 800 nm as detailed below,[14] then strongly reducing resonance contributions to the second-order NLO response of this compound as evaluated by harmonic light scattering measurements at 1907 nm. Satisfactory elemental analysis result was obtained for the target bis(porphyrinato) terbium double-decker complex after repeated column chromatography followed by recrystallization. Its MALDI-TOF mass spectrum clearly shows intense signal for the corresponding protonated molecular ion [M + H]$^+$. The isotopic pattern closely resembles the simulated one, Fig. S1 and Table S1 (ESI†). Nevertheless, this compound was further characterized with a range of spectroscopic techniques including IR and electronic absorption spectroscopy.

The electronic absorption spectrum of HTb(DADAPor)$_2$ was recorded in CHCl$_3$ and shown in Fig. 1, with corresponding data summarized in Table S2 (ESI†). As can be seen, the electronic absorption spectrum of HTb(DADAPor)$_2$ shows a typical Soret band at 445 nm and a weak, broad Q band at 660 nm. No near-
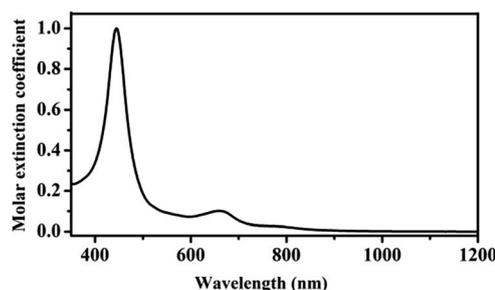

Fig. 1 Electronic absorption spectrum of HTb(DADAPor)$_2$ in CHCl$_3$.

IR absorption band was observed for this homoleptic double-decker, indicating the protonated nature of this double-decker in the form of HTb(DADAPor)$_2$ and, consequently, the off-resonant nature for the first hyperpolarizability of this material.

In the IR spectrum of HTb(DADAPor)$_2$, Fig. S2 (ESI†), the absorption due to the symmetric stretching vibration of the –C≡C– groups is observed at about 2348 cm^{-1}. This is close to the band observed at 2351 cm^{-1} for metal free porphyrin. However, due to the removing of seven of the eight inner pyrrole hydrogen atoms in the bis(porphyrinato) terbium double-decker compound and the significantly decreased interaction of the remaining hydrogen atom (which tautomerises around the four pyrrole nitrogen atoms of one of the two porphyrins in the double-decker molecule[15]) with the pyrrole nitrogen atoms, only a very weak absorption for the characteristic N–H stretching vibration of pyrrole moiety was observed around 3310 cm^{-1}, instead of the relatively intense band usually observed for standard porphyrins.

In spite of several attempts, it was not possible to obtain HTb(DADAPor)$_2$ single crystals suitable for X-ray diffraction analysis. As a consequence, to provide information about the molecular configuration of this double-decker compound, theoretical calculations have been performed to optimize the molecular geometry. As shown in Fig. 2, topology analysis for the molecular skeleton was carried out on the basis of DFT calculation results. Instead of a standard cubic structure, the present bis(porphyrinato) terbium double-decker molecule actually displays a twisted cuboid structure with along x/y edge of 15–16 Å and a short z edge of 4–5 Å, with a twisting angle of 17°, leading to a decrease in the molecular symmetry from the T_d point group for a model cubic octupolar structure to the D_2 point group for the present twisted cuboid octupolar one.

In order to clarify the effect of the widespread π–π interactions within HTb(DADAPor)$_2$ on the molecular structure, reduced density gradient (RDG) analysis was carried out. As clearly exhibited in Fig. 3, π–π interactions in this double-decker molecule exist not only between the two tetrapyrrole chromophores but also between the peripheral donor and acceptor substituents of different porphyrin ligands. Careful inspection over the π–π interactions among the peripheral substituents gives further detailed information about the interaction between π^1[–C≡C–(C$_6$H$_4$)–(C=O)–O–CH$_3$] of one porphyrin and π^2[–(C$_6$H$_4$)–N–(C$_6$H$_5$)$_2$] of the other porphyrin in the double-decker molecule, including a π^1(C≡C)···π^2(C$_6$H$_4$) pair, a π^1(C$_6$H$_4$)···π^2(NC$_3$) pair,
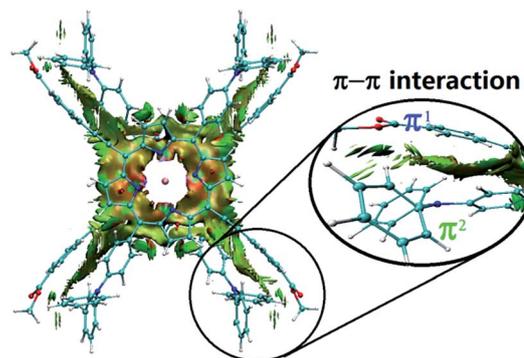
Fig. 3 The widespread π–π interactions within the double-decker molecule of HTb(DADAPor)$_2$.

and a π^1(C=O)···π^2(C$_6$H$_5$) pair. In addition, σ(–CH$_3$) at the end of the π^1 system is also attracted by π^2(C$_6$H$_5$) via the n–π interaction. As a result, these two peripheral aromatic substituents get close to each other with a distance between 3.5 and 4.0 Å. This in turn results in a twisted cuboid octupolar molecular structure with a decreased molecular symmetry of D_2 employed by HTb(DADAPor)$_2$ as shown in Fig. 2.

For this sandwich-type octupolar chromophore of HTb(DADAPor)$_2$, we determine its molecular first hyperpolarizability β (for 1907) by harmonic light scattering[16a] (HLS, also named hyper-Rayleigh scattering[16b]) experiments in chloroform solution. The incident and harmonic wavelengths at 1907 and 953 nm, respectively, are quite remote from the main absorption band of the molecule, then minimizing resonance contributions to the β tensor. Considering these conditions, we report here a very large off-resonant first hyperpolarizability with a value of 1700 × 10^{-30} esu. If we neglect the contribution of the weak Q band around 660 nm, we may apply the two-level dispersion model[16b] to infer a "static β(0) value of 1300 × 10^{-30} esu.

It is worth noting that the sandwich-type bis(ph-thalocyaninato) lutetium double-decker complex Lu(Pc*)$_2$ shows a higher second-order NLO response at 1907 nm, β_{HLS} = 5750 × 10^{-30} esu.[5] However, direct comparison is definitely not appropriate because of the presence of several absorption bands in the visible-near IR range for Lu(Pc*)$_2$ associated with the presence of one unpaired electron in the double-decker molecule.[13] This reveals the significant contribution of a multi-level resonance enhancement to the high β value of Lu(Pc*)$_2$, contrary to our present case where HTb(DADAPor)$_2$ does not show any strong absorption in visible or near-IR region beyond the Soret band due to its reduced protonated nature.[14] This results in a resonance-free first hyperpolarizability for HTb(DADAPor)$_2$ as measured at 1907 nm. On the basis of other off-resonant β_{HRS} values reported thus far for most octupolar NLO materials, which are smaller than 10^3 × 10^{-30} esu,[3–5] the present result therefore represents the largest resonance-free first hyperpolarizability for octupolar molecular materials.

It must be pointed out that according to the geometry inferred from molecular modelling, the twist angle between the two porphyrin derivatives of this double-decker molecule is only 17°, which is much smaller than the value reported in ref. 5 for
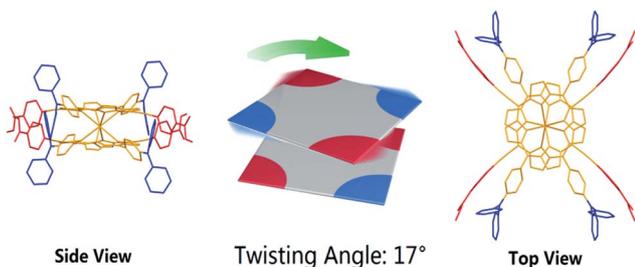

Fig. 2 The simulated molecular structure of HTb(DADAPor)$_2$ with a twisted octupolar cuboid skeleton and the group point of D_2.

Side View   Twisting Angle: 17°   Top View

phthalocyanine derivatives. If this trend could be confirmed by experimental structure determination, the present porphyrine-based strategy opens the ways to the synthesis of T_d – symmetry "perfect octupoles with a real cubic geometry. Further effort towards designing and synthesizing novel bis(tetrapyrrole) rare earth compounds with further enhanced resonance-free second-order NLO response is in progress.

Briefly summarizing above, a novel metal free porphyrin featuring a crosswise DADA arrangement for the electron-donating and electron-withdrawing groups at the four *meso*-positions was designed, synthesized, and employed to construct a bis(porphyrinato) terbium double-decker complex with octupolar molecular symmetry. This, in combination with the intense intramolecular π–π interaction and the lack of any absorption beyond 800 nm in the double-decker molecule, results in the largest off-resonant first hyperpolarizability as evaluated by harmonic light scattering measurements with $\sqrt{(\beta_{HLS}^2)}_{1907} = 1700 \times 10^{-30}$ esu.

Experimental section

General remarks

4-(Diphenylamino)benzaldehyde and methyl 4-bromobenzoate were purchased from Aladdin Inc. CuI, bis(triphenylphosphine) palladium(ɪɪ) dichloride, and trimethylsilylacetylene were bought from Energy Chemical Inc. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200–300 mesh) with the indicated eluents. All other reagents and solvents were used as received. The compounds of methyl 4-ethynylbenzoate[17] and metal free [5,15-dibromo-10,20-(4-diphenylamino)phenyl] porphyrin[18] were prepared according to the literature procedures.

The ^{1}H NMR spectra were recorded on a 400 MHz spectrometer in CDCl$_3$ with shifts referenced to SiMe$_4$ (0.00 ppm). MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance (FT-IR) mass spectrometer with alpha-cyano-4-hydroxy cinnamic acid as the matrix. Elemental analyses were performed on an Elementar Vavio El III. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer in CHCl$_3$ solution at ambient temperature.

Synthesis of metal free [5,15-bis(4-carboxymethyl-phenylethynyl)-10,20-bis(4-diphenylamino)phenyl]porphyrin H$_2$(DADAPor)

The mixture of metal free [5,15-dibromo-10,20-(4-diphenylamino) phenyl]porphyrin (238 mg, 0.025 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.165 mg, 0.24 mmol), and CuI (0.58 mg, 0.31 mmol) in 20 mL dry THF was stirred at 50 °C under nitrogen for 2 h. The precipitate was removed by filtration and the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column using CHCl$_3$/*n*-hexane ether (2 : 1) as eluent. After evaporating the solvent under reduced pressure, the target compound was obtained as a greenish brown solid, 186 mg (67%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.652–0.670 (d, 6H, CH$_3$O$^-$); 7.05–7.46 (d, 20H, Ph); 8.05–8.46 (d, 8H, Ph), 9.058 (d, 2H, pyrolle-H), 9.65 (d, 2H, pyrolle-H). MALDI-TOF MS: an isotopic cluster peaking at m/z 1116.63 [M + H]$^+$; calculated for C$_{76}$H$_{52}$O$_4$N$_6$,

1115.54. Anal. calcd (%) for H$_2$(DADAPor)·(H$_2$O)$_2$·(CH$_3$OH): C, 81.99; H, 4.71; N, 7.55; found: C, 81.58; H, 4.92; N, 7.91.

Synthesis of HTb(DADAPor)$_2$

A mixture of metal free porphyrin (127.6 mg, 0.11 mmol) and Tb(acac)$_3$·nH$_2$O (25.0 mg, 0.021 mmol) in TCB (2.0 mL) was heated to reflux under a nitrogen atmosphere for about 8 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with CHCl$_3$ and methanol (2 : 1 v/v) as the eluent. After the first green band containing unreacted porphyrin, a brown band containing mainly the target double-decker compounds was collected. Repeated chromatography followed by recrystallization from CHCl$_3$ and CH$_3$OH gave a purple powder with the yield of 25%. MALDI-TOF MS: an isotopic cluster peaking at m/z 2397.55 [M + H]$^+$; calculated for C$_{152}$H$_{100}$O$_8$N$_{12}$TbH, 2396.41. Anal. calcd (%) for HTb(DADAPor)$_2$: C, 76.66; H, 4.23; N, 7.06; found: C, 76.84; H, 4.62; N, 7.25.

Calculation summary

Long-range corrected density functional method ωB97XD is employed for geometric calculation.[19] The basis sets of 6-311+G(d) and SDD are employed for C/N/H/O and Tb, respectively.[20] The π–π interactions are plotted using the reduced density gradient (RDG) at the same level.[21] All the calculations were carried out using Multiwfn 3.2 (ref. 22) and Gaussian 09 D.01.[23] Computational details are given in ESI.†

HLS measurements

Hyper-Rayleigh Scattering (HRS) experiment[16] is based on a two-photon scattering process, in which the intensity of the second harmonic scattered light, generated by focusing an intense laser beam onto an isotropic solution, is measured as a function of the incoming laser intensity. Measurements were performed at an IR incident wavelength (1907 nm) chosen to minimize the frequency dispersion of molecular hyperpolarizabilities. A 10^{-5} M solution of chromophore HTb(DADAPor)$_2$ in CHCl$_3$ was prepared and passed through 0.2 μm filters to remove any particles or dust. The experiments was performed at a low chromophore concentration where the linearity of the HRS signal for HTb(DADAPor)$_2$ as a function of chromophore concentration confirmed that no significant aggregation of NLO molecules occurred in this experiment.

Acknowledgements

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