FULL PAPER

Synthesis and Nonlinear Optical Properties of Fluorine-Containing Naphthalocyanines

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Abstract: The fluorine-containing metal naphthalocyanines [F_{16}NcGaCl] (**7**) and [$(F_{16}$NcGa$)_2$O] (**8**), which represent the first examples of peripherally fluorine substituted naphthalocyanines, were synthesized, and the nonlinear optical transmission was studied. Peripheral substitution by fluorine atoms enhances the solubility and photostability of the naphthalocyanines. In particular, for the axially μ-oxo-bridged naphthalocyanine dimer **8**, practically no aggregation was observed in organic solvents and it has proved to be an efficient optical limiter when irradiated with laser light pulses at the wavelength of 532 nm, with pulse duration of 5 ns and repetition rate of 20 Hz.

Keywords: fluorine · gallium · naphthalocyanine · nonlinear optics

Introduction

Since their invention in 1960s,[1] lasers are extensively investigated and used as a high-intensity light sources in optical communication,[2] optical storage,[3] image processing,[4] environmental monitoring,[5] surgery,[6] and military applications.[7] The need for protection of optical sensors and human eyes from accidental or hostile lasers has since then received increasing attention.[7] In particular, it is of great importance to develop passive optical limiters, which respond on the ns or ps timescale, to protect sensors and human eyes from intense laser pulses. In recent years, many materials have been proposed and developed to meet this challenge,[8] including porphyrins,[9] phthalocyanines,[10] fullerenes,[11] organometallic compounds,[12] and indanthrone dyes.[13] Among them, phthalocyanines are especially attractive because of their great reverse saturable absorption (RSA) properties, displaying relatively low linear absorption (or high transmittance) for light of low intensity, but high absorption (or low transmittance) for intense light. However, in order to meet the stringent requirement for sensors or human eye protectors, in addition to be good optical limiters over the entire operating wavelength band of the sensor system, the materials should also have good thermal and photo stability, as well as good processability. Nevertheless, few materials have been developed so far with satisfactory physical properties as well as optical performances in protecting the human eye or an optical sensor. Phthalocyanine-based materials, though among the best materials, are still being investigated to improve their optical-limiting properties and to expand their optical-limiting window from visible to near IR range.[14]

Recently, we found that naphthalocyanine (Nc)-based materials are also promising for optical-limiting applications owing to their expanded ring structure and red-shifted transmission window.[14] Their more extended π-electron systems provide more pronounced nonlinear optical properties than that in the phthalocyanine (Pc) analogues, due to the higher levels of electronic susceptibility.[15] Also, their Q-bands are shifted to the near IR at about 800 nm, and the hue of Nc solutions are thus determined by the B-band absorption in the blue region at about 400 nm. We have successfully synthesized a series of In^{III}–Ncs in attempt to meet the above requirements by increasing their solubility in organic solvents, decreasing aggregation, and thus maintaining their long lifetime of the excited state and good optical-limiting properties.[16, 17] Attempts to obtain Ncs with improved photostability are still on-going.

We report here on a novel approach for Nc modification, namely introducing fluorine atoms on the peripheral positions of the Nc ring. Fluorine substituents are known to enhance the solubility of, for example, Pc,[18] in common organic solvents, and, moreover, it is expected that the electron-withdrawing character of fluorine substituents may improve the photostability of the electronrich Nc rings against photoinduced oxidation. Furthermore, our recent results have demonstrated

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that the solubility could be increased and the aggregation could be prevented by introducing suitable peripheral as well as axial substituents in Pc or Nc compounds, for example, [tBu₄PcGa(p-tmp)],[19] [(tBu₄PcGa)₂O], [(tBu₄PcIn)₂O],[20] [(tBu₄NcGa)₂O],[21] and [{tBu₄PcIn(tmed)}₂].[22] All of these materials have shown promising optical-limiting properties in the visible region. Hence, hexadecafluorogalliumnaphthalo-cyanine [F₁₆NcGaCl] (7) was chosen as the target molecule, and the μ-oxo-bridged dimer [(F₁₆NcGa)₂O] (8) was designed to increase the solubility and block the aggregation further. To our knowledge, these two molecules represent the first examples of peripherally fluorine substituted naphthalocya-nines.

Results and Discussion

As a precursor for the synthesis of [F₁₆NcGaCl] (7), 1,2-dicyano-4,5,6,7-tetrafluoronaphthalene (6) was chosen. The synthetic route for 6 is shown in Scheme 1. 1,2,3,4-Tetrafluoro-5,8-dihydro-5,8-N-methylaminonaphthalene (3) was obtained
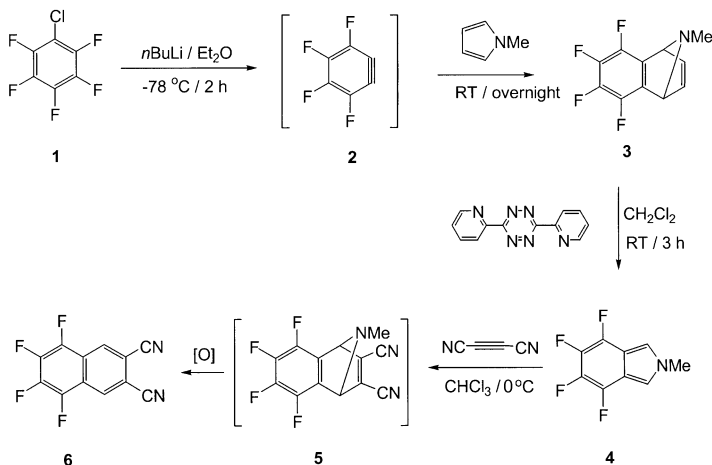
Scheme 1. Synthesis of precursor 6.

from a reaction that was slightly modified based on the published method.[23] The intermediate, tetrafluorobenzyne (2), generated from the reaction of n-butyllithium with pentafluorochlorobenzene in diethyl ether, undergoes a Diels–Alder reaction with 1-methylpyrrole smoothly to afford 3 in moderate yield, which is then converted to N-methyl-4,5,6,7-tetrafluoroisoindole (4)[24] by reaction with 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine, leading to the loss of the −CH=CH− moiety. The monomer 6 is then obtained (yield: 66.7%) by reacting N-methyl-4,5,6,7-tetrafluoroisoindole (4) with dicyanoacetylene,[25] followed by the addition of 3-chloro-peroxybenzoic acid to remove the methylamino group (−NMe) in a one-pot reaction. Compound 6 was fully characterized by spectroscopic methods and elemental anal-ysis. The molecular peak of 6 appears at m/z 250.0 in the MS spectrum. In the IR spectrum, the absorption at 2236.0 cm⁻¹ is characteristic of the −CN groups. The ¹H NMR signal for the two protons in 6 is located at $\delta = -8.58$ ppm (s) and the ¹⁹F

NMR signals for the fluorine atoms appear at $\delta = -145.0$ (m, 2F) and -148.0 ppm (m, 2F).

The synthesis of [F₁₆NcGaCl] (7) and [(F₁₆NcGa)₂O] (8) is shown in Scheme 2. Compound 7 was obtained by the reaction of 6 with GaCl₃ under N₂ atmosphere at 200 °C for
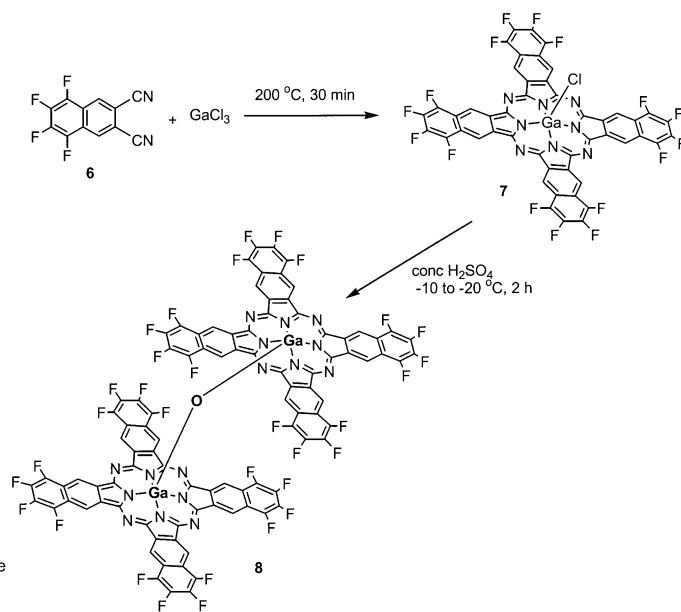
Scheme 2. Synthesis of 7 and 8.

one hour. Compound 7 is slightly soluble in THF. The UV-visible spectrum, exhibiting broad bands, shows that 7 is heavily aggregated in THF (Figure 1). Compared to the peripherally nonsubstituted NcGaCl,[26] which is practically
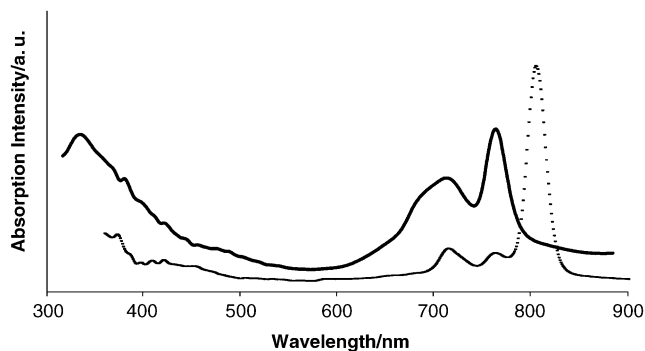

Figure 1. UV/Vis Spectra of 7 in THF (solid line) and 1-chloronaphthalene (dashed line).

insoluble in common organic solvents, the solubility improve-ment for 7, however, is quite significant, confirming that the fluorine atoms do help to improve the solubility. The aggregation in solution can be effectively suppressed when 7 is dissolved in 1-chloronaphthalene, as shown by the sharper absorption bands in its UV-visible spectrum (Figure 1, dashed line). In 1-chloronaphthalene, 7 displays the Q-band at 804.0 nm and the metal-to-ligand/ligand-to-metal charge transfer (MLCT/LMCT) bands at 763.0, 717.0 nm. The MS-

FAB spectrum of **7** shows peaks at $m/z = 1103.8$ $[M^+]$, 1068.9 $[M^+ - Cl]$.

$[(F_{16}NcGa)_2O]$ (**8**) was obtained by the reaction of **7** with concentrated H_2SO_4 at -10 to $-20\,°C$, based on an approach reported by us earlier.[20] The solubility of **8** in common organic solvents is greatly improved when compared to that of **7**. In contrast to **7**, in its UV-visible spectrum, compound **8** has a sharp Q-band at 764.0 nm, the MLCT/LMCT bands at 725.0 and 686.0 nm, and the B-band at 339.0 nm even in THF (Figure 2, solid line). The absorption pattern of **8** is character-
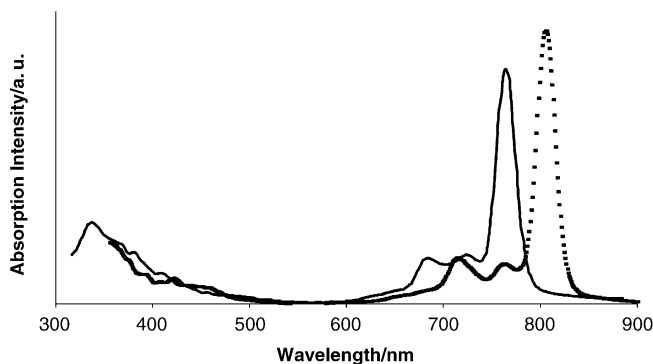

Figure 2. UV/Vis Spectra of **8** in THF (solid line) and 1-chloronaphthalene (dashed line).

istic of Nc derivatives. The UV-visible spectrum is in agreement with our earlier findings that the aggregation can be effectively suppressed by axial substitution.[27] The diminished aggregation of **8** is further demonstrated when its UV-visible spectrum is recorded in 1-chloronaphthalene as solvent (Figure 2, dashed line). The absorption pattern is retained, with a general red-shift of all absorption bands; this is due to the different solvent effect. The field desorption (FD) mass spectrum of **8** shows a single peak at $m/z = 556.9$ $[M^{4+}+H_2O]$, while under FAB mode, the spectrum gives a cluster of peaks centered at $m/z = 2155.2$, which is assigned to $[M^+]$. The ^1H NMR spectrum displays a signal at $\delta = -8.59$ ppm and the ^{19}F NMR signals for the fluorine atoms are found at $\delta = -148.4$ (m, 8F) and -156.5 ppm (m, 8F).

The photostability of **7** and **8** dissolved in THF was checked by comparing the change of their UV-visible spectra before and after light exposure. The intensities of the Q- and B-bands for **7** decreased gradually with increased exposure to daylight for one week without much change in its pattern. The change for **8** under the same conditions is much less significant (Figure 3), thus demonstrating that the dimer is quite stable.

Active materials for optical-limiting display low linear absorption (or high transmittance) for light with low intensity, and high absorption (or low transmittance) for very intense light.[28] For reverse saturable absorption materials, such as naphthalocyanines, this process can be explained by using a simplified four-level model (Figure 4).[29, 30]

When the singlet ground state (S_g) of a molecule passes to the first singlet excited state (S_1) after absorption of a photon emitted by a laser with a pulse width τ, intersystem crossing occurs and the absorbing system converts into the first triplet state (T_1). In the first triplet state T_1, the system can absorb a
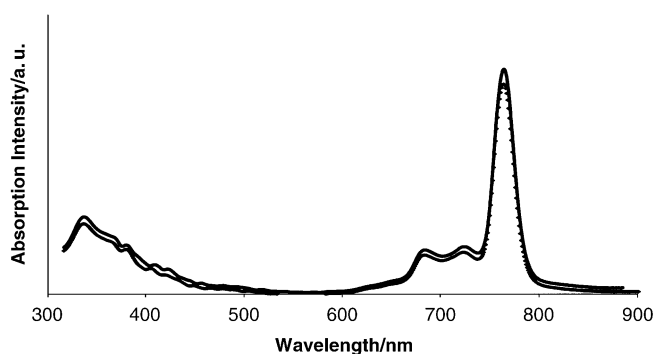

Figure 3. Changes of the UV/Vis absorption spectra of **8** before and after exposure to indoor ambient light: a) before exposure (——), b) after one week (----).
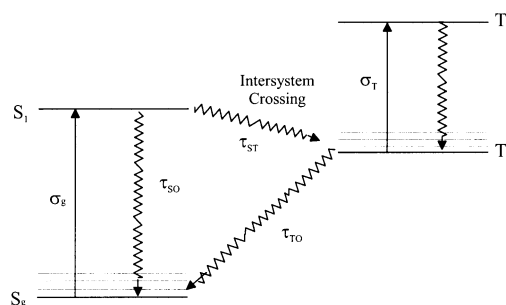

Figure 4. Four-level model of reverse saturable absorption (sequential two-photon absorption).

second photon; this leads the absorbing system to the excited triplet state T_2.

An efficient reverse saturable absorption (RSA) material should have a high ratio of excited-state ($T_1 \rightarrow T_2$) to ground-state ($S_g \rightarrow S_1$) absorption cross section ($\sigma_{ex}/\sigma_g \gg 1$), a rapid intersystem crossing rate ($\tau_{ISC} \ll \tau$), a long internal conversion lifetime ($\tau_{IC} \gg \tau$), a high intersystem crossing quantum yield ($\phi_{S_1 \rightarrow T_1} \sim 1$), and a long triplet lifetime ($\tau_{T_1} \gg \tau$).[31]

Due to the comparable low solubility of $F_{16}NcGaCl$ (**7**), optical limiting was only determined for $(F_{16}NcGa)_2O$ (**8**) in THF (Figure 5). For comparison, optical-limiting measurements were also conducted for C_{60}, $[tBu_4NcGaCl]$,[21] and
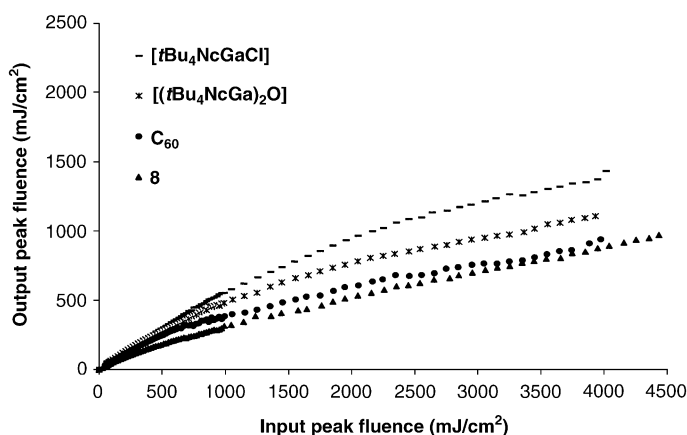

Figure 5. Comparison of the optical limiting performance for various Ncs and $[(F_{16}NcGa)_2O]$ (**8**).

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$[(t\mathrm{Bu_4NcGa})_2\mathrm{O}]$.[21] All of the samples in solution had the linear transmission of 75% at 532 nm. It was found that the optical-limiting performance for **8** is better than that for $\mathrm{C_{60}}$ and the nonfluorinated Nc, $[(t\mathrm{Bu_4NcGa})_2\mathrm{O}]$. The optical-limiting threshold, which is defined as the average input fluence at which the output fluence is 50% of what is predicted by the linear transmission, for **8** and $[(t\mathrm{Bu_4Nc\text{-}Ga})_2\mathrm{O}]$ are 450 and 2150 mJ cm^{-2}, respectively (Table 1). As

Table 1. Optical limiting thresholds for the tested materials.

Compounds	Optical limiting threshold [mJ cm^{-2}]
8	450
$\mathrm{C_{60}}$	1248
$[(t\mathrm{Bu_4NcGa})_2\mathrm{O}]$	2150
$[t\mathrm{Bu_4NcGaCl}]$	3945

these two compounds share the basic Nc structure and the same metal (gallium), it is highly possible that they have the similar intersystem crossing rates, internal conversion lifetimes, intersystem crossing quantum yields, and triplet lifetimes. However, due to the electron-withdrawing effect of the fluorine atoms, the Q-bands of **8** are significantly blue-shifted relative to those of $[(t\mathrm{Bu_4NcGa})_2\mathrm{O}]$.[32] Apparently, their difference in the ground state absorption, and probably the excited state absorption too, leads to a different ratio of their excited-state $(T_1 \rightarrow T_2)$ to ground-state $(S_g \rightarrow S_1)$ absorption cross section (σ_{ex}/σ_g). Based on the optical-limiting measurement results, the ratio of effective σ_{ex}/σ_g for **8** is higher than that for compound $[(t\mathrm{Bu_4NcGa})_2\mathrm{O}]$. Comparable results were also found with fluorinated metal Pcs, which also showed increased effective σ_{ex}/σ_g ratio in comparison with the nonfluorinated Pcs.[33] The improvement was attributed to the augmentation of the difference of the dipole moment between the excited states associated with the optical transition responsible for the optical-limiting effect.

Conclusion

In conclusion, we have synthesized and characterized the hexadecafluoronaphthalocyanine materials, $[\mathrm{F_{16}NcGaCl}]$ (**7**) and $[(\mathrm{F_{16}NcGa})_2\mathrm{O}]$ (**8**), which are the first examples of peripherally fluorine-substituted Ncs. Our results have shown that the solubility and photostability of these new Ncs can be significantly improved by the introduction of fluorine atoms on the peripheral positions of the Nc ring. The high photostability of **7** and **8** is attributed to the electron-withdrawing property of the fluorine atoms, which reduce the electron density in the Nc ring and make its oxidation more difficult when irradiated. We have again demonstrated that the axial dimeric Nc system, represented here by compound **8**, is effective in improving the solubility and suppressing aggregation. In fact, no observable aggregation was found for **8** in THF. The high solubility of **8** in THF allowed the measurement of its optical limiting property at 532 nm in solution. Compound **8** displayed a better optical-limiting performance than $\mathrm{C_{60}}$ and the nonfluorinated $[(t\mathrm{Bu_4NcGa})_2\mathrm{O}]$. At a

molecular level, the cause of the enhanced optical-limiting behavior in **8** is probably due to the involvement of the strong electron-attracting nature of the fluorine substituents, improved dipole moments and a higher effective σ_{ex}/σ_g ratio.

Experimental Section

General: All syntheses were carried out under nitrogen atmosphere. FT-IR: Perkin–Elmer Spectrum 1000, UV/Vis: Shimadzu UV-365, MS: Varian Mat 711 (FD: temperature of the ion source: 30 °C; FAB: temperature of the ion source: 50 °C), ^{1}H and ^{19}F NMR: Bruker Avance DRX 250 (235.334 MHz).

1,2,3,4-Tetrafluoro-5,8-dihydro-5,8-*N*-methylaminonaphthalene (3):[23] *n*-Butyllithium (1.6 M in hexane; 27.5 mL, 44.0 mmol) was added dropwise to a magnetically stirred solution of **1** (5.2 mL, 40.0 mmol) in dry Et$_2$O (100 mL) under N$_2$ at −78 °C. The solution was stirred for 1 h at −78 °C and then treated dropwise with 1-methylpyrrole (14.4 mL, 80.0 mmol). The mixture was further stirred for 1 h at that temperature and then allowed to warm slowly to room temperature and stirred overnight. The brown solution obtained was washed with 4 N H$_2$SO$_4$ (3 × 50 mL), and the aqueous layer was basified with 4 N NaOH and extracted with Et$_2$O (3 × 100 mL). The organic layer was dried over NaSO$_4$, evaporated to afford crude **3**, which was purified by crystallization from *n*-hexane: white crystals, 4.6 g, yield: 50.2%, m.p. 74.5–76.0 °C (lit. [23] m.p. 75–76 °C).

N-Methyl-4,5,6,7-tetrafluoroisoindole (4):[24] 3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine (472.0 mg, 2.0 mmol) was added in one portion to a magnetically stirred solution of **3** (458.0 mg, 2.0 mmol) in CH$_2$Cl$_2$ (40 mL). The resulting magenta solution was stirred for 3 h at room temperature. The solution was then evaporated and purified by chromatography on neutral Al$_2$O$_3$ with CH$_2$Cl$_2$ as eluent to give **4**: 340.0 mg, 83.7%, m.p. 176–177.5 °C (lit. [24] m.p. 178 °C).

1,2-Dicyano-4,5,6,7-tetrafluoronaphthalene (6): Dicyanoacetylene[25] (114.0 mg, 1.5 mmol) was added slowly to a magnetically stirred solution of **4** (305.0 mg, 1.5 mmol) in CHCl$_3$ (20 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. 3-Chloroperoxybenzoic acid (77% max; 656.5 mg, ∼3.0 mmol) was added in one portion, and the mixture was stirred at room temperature overnight. The solution was washed with aqueous NaOH solution (2 N, 50 mL × 3, to remove 3-chlorobenzoic acid) and water (50 mL × 3), and then dried over Na$_2$SO$_4$. After evaporation, the residue obtained was subjected to flash chromatography on silica gel with CHCl$_3$ as eluent to yield **6**: 250.0 mg, 66.7%, m.p. 215–216.5 °C; MS (*m/z*): 250.0 [M^+]; ^{1}H NMR (CDCl$_3$): $\delta = 8.58$ ppm (s); ^{19}F NMR (CDCl$_3$, C$_6$H$_5$CF$_3$ as reference): $\delta = -145.0$ (m, 2F), -148.0 ppm (m, 2F); IR (KBr): $\tilde{v} = 2236.0$ cm^{-1} (−CN); elemental analysis calcd (%) for C$_{12}$H$_2$N$_2$F$_4$: C 57.62, H 0.81, N 11.20, F 30.38; found: C 57.82, H 0.61, N 11.30, F 30.80.

[F$_{16}$NcGaCl] (7): Compound **6** (100.0 mg, 0.4 mmol) and GaCl$_3$ (176.0 mg, 1.0 mmol) were mixed and heated to 200 °C for 1 h. The reaction mixture was dissolved in 1-chloronaphthalene and added dropwise into methanol (100 mL). The precipitate was collected and washed with methanol to give a dark blue product (40.0 mg, 36.2%). MS-FAB (*m/z*): 1103.8 [M^+], 1068.9 [M^+ − Cl]; IR (KBr): $\tilde{v}$ 1655.0 (m), 1606.0 (m), 1498.0 (vs), 1377.0 (vs), 1129.0 (s), 1093.0 (s), 1068.0 (w), 996.0 (vs), 972.0, (vs) 893.0 (w), 862.0 (w), 809.0 (w), 760.0 (w), 742.0 (w), 681.0 (m), 639.0 (w), 512.0 (w), 494.0 (w), 440.0 cm^{-1} (w); UV/Vis (THF): $\lambda_{max} = 765.0$, 718.0, 338.0 nm; UV/Vis (1-chloronaphthalene): $\lambda_{max} = 804.0$, 763.0, 717.0 nm; elemental analysis calcd (%) for C$_{48}$H$_8$ClGaN$_8$F$_{16}$: C 52.16, H 0.73, N 10.14, Cl 3.21; found C 49.62, H 0.90, N 9.61, Cl 3.23.

[(F$_{16}$NcGa)$_2$O] (8): Compound **7** (40.0 mg, 0.018 mmol) was dissolved in conc. H$_2$SO$_4$ (20 mL) at −10 to −20 °C and stirred for 2 h. The dark blue reaction mixture was quenched with ice-water (200 mL), filtered, and dried to obtain a dark green solid (18.0 mg, 46.0%). MS-FD (*m/z*): 556.9 [M^{4+}+H$_2$O]; MS-FAB (*m/z*): 2155.2 [M^+]; IR (KBr): $\tilde{v}$ = 1655.0 (m), 1604.0 (m), 1496.0 (vs), 1377.0 (vs), 1189.0 (w), 1130.0 (s), 1094.0 (s), 1068.0 (w), 996.0 (vs), 977.0 (vs), 897.0 (w), 864.0 (w), 810.0 (w), 763.0 (w), 745.0 (w), 682.0 (m), 640.0 (w), 516.0 (w), 439.0 cm^{-1} (w); UV/Vis (THF): $\lambda_{max} = 764.0$, 725.0, 686.0, 339.0 nm; UV/Vis (1-chloronaphthalene): $\lambda_{max} = 805.0$, 763.0, 716.0, 339.0 nm; ^{1}H NMR ([D$_8$]THF): $\delta = 8.59$ ppm (s); ^{19}F NMR

([D$_8$]THF, C$_6$H$_5$CF$_3$ as reference): $\delta = -148.4$ (m, 8F), -156.5 ppm (m, 8F). elemental analysis calcd (%) for C$_{96}$H$_{16}$Ga$_2$F$_{32}$N$_{16}$O: C 53.50, H 0.75, N 10.40; found: C 51.02, H 0.94, N 9.26.

Optical-limiting measurement: The optical-limiting experiments were conducted by using a laser light with wavelength of 532 nm, a pulse duration of 5 ns, and a repetition rate of 20 Hz. The pulses were generated by a frequency-doubled Q-switched Nd/YAG laser. A small part of the input beam was split by using a glass plate to monitor the input energy. The major part of the laser beam was focused with a lens with a focal length of 250 mm, and the sample was placed near the focus point ($\sim$100 μm in diameter). After propagation through the medium, the major portion of the beam was collected by a photodiode detector. This allowed a direct measurement of the nonlinear absorption properties. Other mechanisms leading to light dispersion, such as photon diffusion or nonlinear refraction, were not taken into account.[30] The transmission for each sample was measured at several different incident fluences varying from 10 mJ cm^{-2} to 4000 mJ cm^{-2}. The data points are obtained by averaging the measurements of around 40 shots. The tested samples were prepared as solutions and all had $75 \pm 1\%$ of linear transmission at 532 nm. Their optical-limiting performance at 532 nm was evaluated and compared based on their limiting thresholds, which is defined as the average input fluence at which the output fluence is 50% of what is predicted by the linear transmission. C$_{60}$ was included and was dissolved in toluene in a quartz cell with 1 mm thickness. The rest of the samples were dissolved in THF and tested in the same type of optical cells.

Acknowledgement

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