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Tuning Octopolar NLO Chromophores: Synthesis and Spectroscopic Characterization of Persubstituted 1,3,5-Tris(ethynylphenyl)benzenes

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The synthesis of a series of octopolar 1,3,5-tris(ethynylphenyl)benzenes via Sonogashira coupling is described, varying the substituents on both the central benzene core as well as the acetylenic periphery. In particular, systems bearing an electron-rich core and an electron-poor periphery are obtained that display advanced optical properties. The linear (by UV–vis and fluorescence spectroscopy) and second-order nonlinear optical properties are studied, the latter by hyper-Rayleigh scattering (HRS) (Hendrickx, E.; Clays, K.; Persoons, A. *Acc. Chem. Res.* **1998**, *31*, 675–683). The influence of different core and periphery substitution is revealed by the optical properties and confirms the possibility of fine-tuning those. Because of the presence of (one-photon) fluorescence for all compounds, femtosecond hyper-Rayleigh scattering has been applied (Olbrechts, G.; Strobbe, R.; Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1998**, *69*, 2233–2241). The implementation of the deconvolution in the frequency domain allows for a demodulation and a phase shift between immediate (nonlinear) scattering and time-delayed (multiphoton) fluorescence for high modulation frequencies (Wostyn, K.; Binnemans, K.; Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **2001**, *72*, 3215–3220). In accordance with the linear optical properties, the second-order NLO properties can also be tuned by varying the core and peripheric substitutents.

Introduction

The growing field of molecular photonics and electrooptics has created a great demand for nonlinear optic (NLO) materials that can be individually adapted to the requirements set by a particular application.[4] In this context, organic molecules appear as promising candidates since their molecular properties can be tuned to an almost infinite extend via organic synthesis.[5] On the macroscopic level, crystal engineering and supramolecular chemistry can give access to molecular materials and devices based on suitably prefunctionalized organic molecules.[6] This transition from single second-order NLO-active molecules, most commonly conjugated dipolar systems, to the supramolecular arrangement in the bulk material led to problems, namely the extinction of the macroscopic susceptibility due to antiparallel alignment of the molecules. This directed increasing attention to molecular octopoles. Octopolar molecules, possessing a zero overall dipole moment, can ideally be oriented in the bulk phase in a way that their molecular susceptibility is additive.[7]

A common way to design second-order NLO-active octopolar molecules is to synthesize noncentrosymmetrically substituted trigonal or tetrahedral π-conjugated systems that display efficient charge transfer (CT) from the periphery to the center of the molecule.[8] Acetylenic systems constitute among octopolar NLO chromophores with the highest second-order polarizabilities known so far. A small number of alternatingly persubstituted trisethynylbenzenes has been described in the literature

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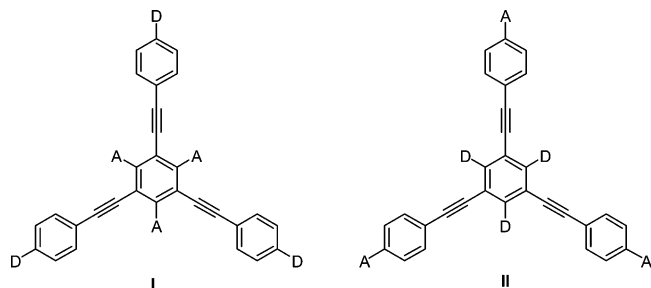
FIGURE 1. Donor−acceptor-substituted 1,3,5-tris(arylethynyl)benzenes.

with donor substitution on the periphery and acceptor substituents on the center (type I, Figure 1).[9] However, to the best of our knowledge, there are no such systems reported which possess an electron-rich benzene core and an electron-poor periphery (type II, Figure 1).

Yet, it is highly desirable to be able to control and vary both the peripheric as well as the central aryl substituents in order to allow for a versatile electronic or structural tuning of the target compounds. In the design of NLO materials, secondary interaction sites can be used to direct the alignement of the respective molecules, as has been recently demonstrated for liquid crystal materials.[10] Furthermore, in the context of dendritic systems,[11] where most commonly energy transfer takes place in a directed manner from the outer rim to a central unit or in an undirected fashion,[12] covalent tuning of the respective building blocks in a way suggested here would put a handle on the problem of directing energy transfer (CT, respectively) in the desired way.

Results and Discussion

Synthesis. In light of sometimes cumbersome product isolation from Stille couplings[10a] and low yields due to statistical mixtures in cyclotrimerizations,[8a,9b] the Sonogashira coupling figures as the most obvious choice for the synthesis of 1,3,5-trisalkynylbenzenes. In a recent communication, we reported a synthetic procedure to obtain C_3-symmetric trisalkynylbenzenes via Sonogashira coupling. However, in this case an "optimal" substrate, the electron-poor aryliodide **1c**, was employed in the coupling step.[13] Here, we describe the synthesis of 2,4,6-substituted 1,3,5-trisethynylbenzene derivatives with different substituents on the central benzene core as well as on the phenylethynyl periphery, in particular yielding systems with electron-rich benzene cores.

Due to synthetic−mechanistic considerations, it is in general strongly disadvantageous to use sterically hindered electron-rich aryl halides in palladium-catalyzed cross-coupling reactions to obtain such systems.[14] Nevertheless, choosing from the plethora of reported methods,[15] the 1,3,5-trisethynylbenzenes **2**−**4** could be obtained in modest to good yields from the 1,3,5-triiodobenzenes[16] **1a**−**c** and commercially available ethynylbenzene derivatives using standard Sonogashira coupling conditions (Scheme 1).[17]

For the sake of generality, the reaction conditions, which have been found to be most appropriate for the least reactive triiodobenzene **1a**, have been applied to all other coupling reactions without further individual optimization. The ethynyl starting material had only little influence on the reaction time and yield. However, it should be noted that especially the strongly activated triiodo compound **1c** could be reacted much faster and at significantly lower temperature.[13]

Linear Spectroscopy. Regarding their spectroscopic behavior, the trimethyl-, trimethoxy-, and trifluorobenzenes show in general the same following tendencies: An absorption band of lower intensity around 234 nm remains relatively unaffected by varying the substituents in the molecule center and its acetylenic periphery. A main absorption band can be observed between 290 and 303 nm with a shoulder of lesser intensity between 310 and 318 nm, corresponding to the phenylacetylene chormogenic unit,[18] which both shift bathochromically with increasing electron density in the central benzene core (F < CH_3 < OCH_3). Since meta-substitution disrupts conjugation in simple phenylacetylene systems,[19] this effect can be directly related to an increase in the CT-character as a result of the substitution pattern and not of increasing conjugation length. It is also obvious that the peripheric aryl substituents are less influencial on the spectroscopic properties compared to the core-substitution as can be deduced by comparing benzenes having the same core substitution with those carrying the same peripheric substituents (Table 1, Figure 2).

The same trend can be observed even more pronounced by looking at the compounds' fluorescence properties. The modestly broadened, unstructured emission band, located between 358 and 380 nm for all compounds, is significantly red-shifted for the trismethoxybenzenes **2a**, **3a**, and **4a**, compared to their trimethyl and to an even stronger extent to their trifluoro analogues. Figure 2 shows a difference in the emission maxima of **4a** and **4c** of 22 nm. Comparing the fluorescence quantum yields, the trifluorobenzenes display the smallest values (0.14−0.18) while those of the trimethyl- and trimethoxybenzenes are in the same order of magnitude, between 0.21 and 0.29. In all cases, the observed Stokes shifts are large and reach a maximum of 80 nm for compound **4a**.

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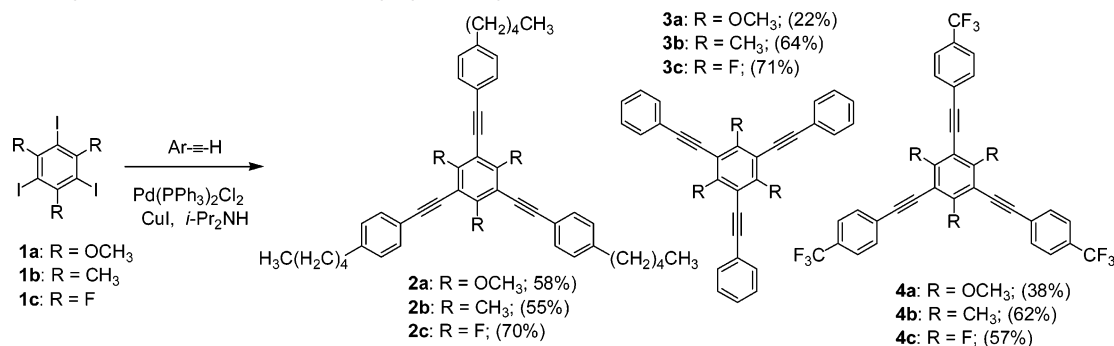**SCHEME 1. Synthesis of 1,3,5-Tris(ethynylphenyl)benzenes 2−4**

TABLE 1. Linear and Nonlinear Optical Properties of Compounds 2−4

		1,3,5-tris[(4-pentylphenyl)-ethynyl]- (2)	1,3,5-tris(phenyl-ethynyl)- (3)	1,3,5-tris[(4-trifluoromethyl-phenyl)ethynyl]- (4)
-2,4,6-trimethoxybenzene (**a**)	$\beta_{HRS,800nm}{}^{a}$	37 ± 2	34 ± 3	39 ± 5
	$\beta_{HRS,0}$	11.5 ± 1	11 ± 1	13 ± 2
	$\lambda_{max,abs}$	318	317	317
	$\lambda_{max,em}$	376	375	380
	Φ^{b}	0.27	0.21	0.25
-2,4,6-trimethylbenzene (**b**)	$\beta_{HRS,800nm}{}^{a}$	32 ± 2	18 ± 2	45 ± 3
	$\beta_{HRS,0}$	10 ± 1	6 ± 1	14 ± 1
	$\lambda_{max,abs}$	317	313	317
	$\lambda_{max,em}$	365	363	365
	Φ^{b}	0.29	0.28	0.25
-2,4,6-trifluorobenzene (**c**)	$\beta_{HRS,800nm}{}^{a}$	25 ± 3	19 ± 2	28 ± 3
	$\beta_{HRS,0}$	8.5 ± 1	6.2 + 1	10 ± 1
	$\lambda_{max,abs}$	310	313	305
	$\lambda_{max,em}$	369	365	358
	Φ^{b}	0.18	0.17	0.14

[a] In units of 10^{-30} esu; absorption ($c = 10^{-6}$ mol L^{-1}) and emission ($c = 10^{-8}$ mol L^{-1}) maxima in nm, spectra recorded in chloroform. [b] Samples excited at 300 nm, quantum yields Φ determined using quinine sulfate ($c = 0.1$ mol L^{-1} in H$_2$SO$_4$) as standard,[20] estimated error ± 10%.
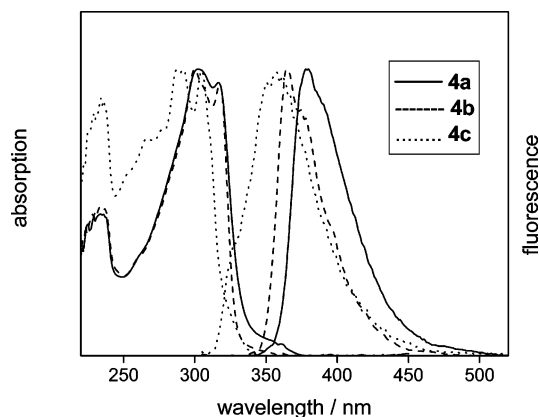

FIGURE 2. Normalized absorption and emission spectra of **4a−c** in chloroform.

Nonlinear Spectroscopy. For all nine compounds, *multi*photon fluorescence was also observed. This is not surprising, since the octopolar molecular motif has also been shown to be beneficial for this third-order nonlinear optical property.[21] However, by simultaneous fitting of the demodulation and the phase data as a function of

modulation frequency toward the fluorescence-free hyperpolarizability, the multiphoton fluorescence contribution and the fluorescence lifetime, an accurate and precise value for the first hyperpolarizability could be obtained. As reference value, 338×10^{-30} esu was used for the $\beta_{333} = -\beta_{311} = -\beta_{131} = -\beta_{113}$ for crystal violet (*3*-axis along the ethynyl bridge, *1*-axis in the plane of the core benzene ring and perpendicular to the *3*-axis, *2*-axis perpendicular to the *13*-plane) in methanol. Since the reference compound has the same octopolar symmetry as the unknowns, no correction factors for the difference between dipolar and octopolar contributions need to be taken into account. The reported hyperpolarizability values are the dynamic values obtained at 800 nm. For charge-transfer bands between 305 and 318 nm, this results in a resonance enhancement factor between 2.80 and 3.23, in the simple two-level model, that is also applicable to octopoles.[22] The resulting static hyperpolarizability values are also given in the table. When considering that the peripheric aryl substitution has only a secondary effect, the degree of fine-tuning that can be realized by different core substitution can be demonstrated by the average static hyperpolarizability value for the trimethoxy- (**a**), the trimethyl- (**b**), and the trifluorobenzenes (**c**), respectively, as 11.8, 10.0, and 8.2 × 10^{-30} esu. Despite this overall tendency, one also has to consider

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the direct comparison of structurally more closely related compounds by varying only the central or the peripheric substitution at a time in order to gain a more accurate idea of how the substitution pattern influences the NLO response. For example, the β-value in the trimethyl series (**2b**−**4b**) is the subject of a significant change, varying from 18 to 45 × 10^{-30} esu.

Conclusion

Straightforward Sonogashira coupling proved to be an efficient and versatile synthetic method to obtain persubstituted 1,3,5-trisethynylbenzenes with octopolar symmetry. It permits the introduction of different substituents on both the acetylenic periphery as well as the central benzene core. The usefulness of chemically tuning the target compounds in such a way has been demonstrated first of all by linear UV−vis and fluorescence spectroscopy where the absorption and emission features can be tailored according to the respective substitution patterns. More interestingly, also from the HRS data it is clear that the nonlinear optical properties can be fine-tuned by the proper functionalization at the periphery and at the core. There is good correspondence between the linear and the nonlinear properties: the stronger effect of the core substitution and the weaker influence of the peripheric aryl substituents are confirmed. The hyperpolarizability values are in a comparable order of magnitude with respect to known octopolar systems[8b,9] and can possibly be further amplified by choosing the appropriate substituents. Rather than targeting maximum second hyperpolarizability values, we would like to emphasize the usefulness and general applicability of the synthetic strategy. Also, a remarkable degree of control of the linear and nonlinear optical response can be obtained by changing the position (periphery/core) and, more importantly, the electronic nature of the phenyl substituents.

Experimental Section

1,3,5-Triiodo-2,4,6-trimethoxybenzene (1a). To a suspension of NaH (0.014 mol, 348 mg of a 60% dispersion in mineral oil) in Et$_2$O (2 mL) was added MeOH (0.014 mol, 0.425 mL) in Et$_2$O (1 mL) dropwise and the mixture stirred for 0.5 h at room temperature. The remaining solvent was blown off in a stream of argon, and DMI (2 mL) and then, portionwise, 1,3,5-trifluro-2,4,6-triiodobenzene were added subsequently. The remaining reaction mixture was stirred under argon at room temperature for 18 h before being poured into hydrochloric acid (0.5 N, 30 mL). The resulting solid was filtered, washed several times with water, and finally recrystallized from MeOH to give pure **1a** as a colorless solid. Yield: 770 mg; 72%. Mp: 163−165 °C. ^{1}H NMR: δ = 3.86 (s, 9 H). ^{13}C NMR: δ = 161.4, 82.6, 60.8. EI$^+$-MS m/z: 546 (100, [M$^+$]). HRMS: found 545.7677, calcd for C$_9$H$_9$O$_3$I$_3$ 545.7686. R_f (TLC) = 0.52 (Hex−EtOAc 20:1).

General Procedure for the Preparation of the 1,3,5-Tris(arylethynyl)benzenes 2a−4c. The 1,3,5-triiodobenzene derivatives **1a−c** (1.0 mmol) was stirred in dry, degassed i-Pr$_2$-NH (10 mL) together with CuI (0.15 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.15 mmol) under argon at room temperature for 0.5 h before the respective arylethynyl compound was added. The mixture was heated at 80 °C for 48 h, the solvent was removed in vacuo, and to the remaining residue was added water (50 mL). After extraction with EtOAc (3 × 30 mL), the combined organic layers were dried (MgSO$_4$) and concentrated in vacuo to give the crude product. After purification via column chromatography or/and recrystallization, the pure products were obtained in yields between 22 and 71%.

1,3,5-Tris[(4-pentylphenyl)ethynyl]-2,4,6-trimethoxybenzene (2a). Pure **2a** was obtained upon column chromatography (1:1 Hex−cyclohexane) as an orange oil. Yield: 213 mg; 58%. R_f = 0.44. ^{1}H NMR: δ = 7.53 (AB, J = 8 Hz, 6 H), 7.22 (AB, J = 8 Hz; 6 H), 4.22 (s, 9 H), 2.66 (t, J = 7.8 Hz, 6 H), 1.66 (m, 6 H), 1.38 (m, 12 H) 0.94 (t, J = 6.3 Hz, 9 H). ^{13}C NMR: δ = 163.0, 143.4, 131.3, 128.4, 120.6, 107.9, 97.6, 80.2, 61.2, 35. 8, 31.3, 30.8, 22.4, 13.9. EI$^+$-MS m/z: 678 (100, [M$^+$]). Anal. Calcd for C$_{48}$H$_{44}$O$_3$: C, 84.96; H, 7.96. Found: C, 84.78; H, 8.21.

1,3,5-Tris[(4-pentylphenyl)ethynyl]-2,4,6-trimethylbenzene (2b). Pure **2b** was obtained upon column chromatography (20:1 Hex−EtOAc) and final washing of the solid with EtOH as colorless crystals. Yield: 346 mg; 55%. Mp: 56 °C. ^{1}H NMR: δ = 7.52 (AB, J = 7.8 Hz, 6 H), 7.22 (AB, J = 7.8 Hz; 6 H), 2.79 (s, 9 H), 2.68 (t, J = 7.8 Hz, 6 H), 1.68 (m, 6 H), 1.38 (m, 12 H) 0.96 (t, J = 6.3 Hz, 9 H). ^{13}C NMR: δ = 143.4, 141.7, 131.3, 128.5, 121.4, 120.8, 97.6, 86.4, 35.9, 31.4, 31.0, 22.5, 20.3, 14.0. EI$^+$-MS m/z: 630 (100, [M$^+$]). Anal. Calcd for C$_{48}$H$_{54}$: C, 91.43; H, 8.57. Found: C, 91.38; H, 8.55.

1,3,5-Tris[(4-pentylphenyl)ethynyl]-2,4,6-trifluorobenzene (2c). Pure **2c** was obtained upon column chromatography (Hex) and final recrystallization from i-PrOH as colorless crystals. Yield: 449 mg; 70%. Mp: 72 °C. ^{1}H NMR: δ = 7.50 (AB, J = 7.8 Hz, 6 H), 7.20 (AB, J = 7.8 Hz; 6 H), 2.64 (t, J = 7.8 Hz, 6 H), 1.63 (m, 6 H), 1.36 (m, 12 H) 0.91 (t, J = 6.3 Hz, 9 H). ^{13}C NMR: δ = 161.8 (d, J_{CF} = 261 Hz), 144.5, 131.8, 128.5, 119.3, 100.0, 73.8, 35.9, 31.4, 30.8, 22.5, 14.0. FAB$^+$-MS: m/z 642 (100, [M$^+$]). Anal. Calcd for C$_{45}$H$_{45}$F$_3$: C, 84.11; H, 7.01. Found: C, 84.55; H, 6.97.

1,3,5-Tris(phenylethynyl)-2,4,6-methoxybenzene (3a). Pure **3a** was obtained upon column chromatography (10:1 Hex−EtOAc) and final recrystallization from cyclohexane as a pale orange solid. Yield: 103 mg; 22%. Mp: 110−111 °C. ^{1}H NMR: δ = 7.57−7.55 (m, 6 H), 7.38−7.36 (m, 9 H), 4.18 (s, 9 H). ^{13}C NMR: δ = 163.4, 131.4, 128.4 123.5 107.8, 97.5 80.9, 61.5. EI$^+$-MS m/z: 468 (100, [M$^+$]). Anal. Calcd for C$_{33}$H$_{24}$O$_3$: C, 84.62; H, 5.13. Found: C, 84.50; H, 5.35.

1,3,5-Tris(phenylethynyl)-2,4,6-methylbenzene (3b).[23] Pure **3b** was obtained upon column chromatography (2:1 Hex−CH$_2$Cl$_2$) and final recrystallization from i-PrOH as an off-white solid. Yield: 267 mg; 64%. Mp: 248−252 °C. ^{1}H NMR: δ = 7.60−7.55 (m, 6 H), 7.41−7.35 (m, 9 H), 2.76 (s, 9 H). ^{13}C NMR: δ = 142.1, 131.4, 128.4, 128.3 123.6, 121.4, 97.4, 86.9, 20.3. EI$^+$-MS m/z: 420 (100, [M$^+$]). Anal. Calcd for C$_{33}$H$_{24}$: C, 94.29; H, 5.71. Found: C, 94.27; H, 5.89.

1,3,5-Tris(phenylethynyl)-2,4,6-trifluorobenzene (3c). Pure **3c** was obtained upon column chromatography (2:1 Hex−CH$_2$Cl$_2$) and final recrystallization from i-PrOH as colorless needles. Yield: 309 mg; 71%. Mp: 184−185 °C. ^{1}H NMR: δ = 7.63−7.58 (m, 6 H), 7.42−7.39 (m, 9 H). ^{13}C NMR: δ = 161.95 (d, J_{CF} = 261 Hz), 131.8, 129.2, 128.4, 122.1, 99.8 74.3. EI$^+$-MS m/z: 432 (100, [M$^+$]). Anal. Calcd for C$_{30}$H$_{15}$F$_3$: C, 83.33; H, 3.47. Found: C, 82.88; H, 3.53.

1,3,5-Tris[(4-trifluoromethylphenyl)ethynyl]-2,4,6-trimethoxybenzene (4a). Pure **4a** was obtained upon column chromatography (5:1 Hex−EtOAc) and final recrystallization from cyclohexane as bright yellow crystals. Yield: 255 mg; 38%. Mp: 108−110 °C. ^{1}H NMR: δ = 7.65 (s, 12 H), 4.19 (s, 9 H). ^{13}C NMR: δ = 164.2, 131.6, 130.5 125.4, 122.1, 118.5, 107.2, 96.3, 83.0 61.7. EI$^+$-MS m/z: 672 (100, [M$^+$]). Anal. Calcd for C$_{36}$H$_{21}$O$_3$F$_9$: C, 64.29; H, 3.13. Found: C, 64.30; H, 3.21.

1,3,5-Tris[(4-trifluoromethylphenyl)ethynyl]-2,4,6-trimethylbenzene (4b). The remaining oily residue was triturated with MeOH. The resulting solid was filtered and recrystallized from CH$_3$NO$_2$ to yield pure **4b** as colorless needles. Yield: 387 mg; 62%. Mp: 268−269 °C. ^{1}H NMR: δ = 7.60 (s, 12 H), 2.73 (s, 9 H). ^{13}C NMR: δ = 143.0, 131.6, 129.9,

127.1, 125.3, 122.1, 121.0, 118.5, 96.3, 88.9, 20.3. EI$^+$-MS *m/z*: 624 (100, [M$^+$]). Anal. Calcd for $C_{36}H_{21}F_9$: C, 69.23; H, 3.37. Found: C, 69.09; H, 3.46.

1,3,5-Tris[(4-trifluoromethylphenyl)ethynyl]-2,4,6-tri-fluorobenzene (4c). Pure **4c** was obtained upon column chromatography (Hex) and final recrystallization from cyclohexane as colorless crystals. Yield: 364 mg; 57%. Mp: 100−104 °C. ^{1}H NMR: $\delta = 7.71-7.58$ (m, 12 H). ^{13}C NMR: $\delta = 162.5$ (d, $J_{CF} = 263.1$ Hz), 132.1, 131.8, 129.2, 125.5, 121.9, 118.3, 98.5, 76.1. EI$^+$-MS *m/z*: 636 (100, [M$^+$]). Anal. Calcd for $C_{33}H_{12}F_{12}$: C, 62.26; H, 1.89. Found: C, 62.74; H, 2.08.

Supporting Information Available: Linear spectroscopic data and general methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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