Diphenyloligothiophene-Based Dichromophoric Macrocycles and Their Ability to Form Donor/Acceptor Complexes

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A series of four dichromophoric rigid macrocycles **6a**−**6d**, two with diphenyloligothiophene chromophores, the other two with more electron-rich diphenyl-EDOT or diphenyl-bis-EDOT chromophores, have been synthesized. The absorption spectrum of the diphenyl-bis-EDOT based macrocycle **6d** displayed the most pronounced vibronic resolution with a well-resolved 0−0 transition, indicating a fully planarized geometry of the diphenyl-bis-EDOT chromophores. The ^{1}H NMR spectra of the macrocycles displayed weak to moderate chemical shifts of characteristic signals upon addition of π-conjugated oligonitro-9-fluorenone acceptors. X-ray single-crystal analysis showed that columnar π-stacked donor/acceptor complexes are formed with the stacks composed of alternating donor and acceptor molecules. The stoichiometry of the crystalline, dark-colored complexes was found to be 1:1 by elemental analysis and integration of the ^{1}H NMR peaks. The complex formation is accompanied by remarkably large Stern−Volmer constants of fluorescence quenching.

Introduction

Intense current interest in the design of multicomponent, nanoscale molecular assemblies has led to the exploitation of many types of intermolecular interaction, including hydrogen bonding,[1] solvophobic effects,[2] metal−ligand coordination,[3] and π-stacking between aromatic donor and acceptor sites.[4] As a promising class of attractive interactions, π-stacking interactions have found to be especially valuable for directing the synthesis of supermolecular systems such as catenanes and rotaxanes[5] and for realizing fluorescence quenching toward sensor applications.[6]

With their promising optical and electronic properties, organic materials based on oligothiophenes have been intensively investigated.[7] Within this line, Köhler et al.[8] described the synthesis and optical/chiroptical properties of a novel rigid macrocycle that contains two diphenylbithiophene chromophores that are fixed by two spirobisindane clips (Figure 1, **6a**). In this work, we extended the collection of such rigid macrocyclic structures by replacing the central bithiophene moiety by terthiophene (Figure 1, **6b**), or by more electron-rich moieties as 3,4-(ethylenedioxy)thiophene (EDOT) (Figure 1, **6c**) and 3,4:3′,4′-bis(ethylenedioxy)-2,2′-bithiophene (bis-EDOT) (Figure 1, **6d**). The now available series of four different macrocycles were tested as potential donors for electron-deficient acceptors (including 2,4,7-trinitro-9-fluorenone, TriNF, and 2,4,5,7-tetranitro-9-fluorenone, TetNF, Figure 1). Studies of the electrochemical behavior of oligonitro-9-fluorenones showed that the electron-accepting ability increases as more nitro groups are present in the molecule. Thus, the half-wave potentials for the electrochemical reduction of oligonitro-9-fluorenones (against an Ag/AgCl reference electrode) increase in the following order: −0.68 V for 2,7-dinitro-9-fluorenone, −0.42 V for 2,4,7-trinitro-9-fluorenone, and +0.14 V for 2,4,5,7-tetranitro-9-fluorenone.[9]

The macrocycles **6a**−**6d** and acceptors have been investigated for their formation of charge-transfer complexes. Elemental analysis of three crystalline, dark-colored donor/acceptor complexes gave a macrocycle/oligonitro-9-fluorenone ratio of 1:1. The NMR analysis of dissolved donor/acceptor mixtures showed only weak ^{1}H NMR shifts of characteristic aromatic protons. Therefore, the formation of highly stabilized inclusion complexes is very unlikely, most probably due to steric reasons. X-ray single-crystal analysis has shown that π-stacked, columnar donor/acceptor complexes are formed with the acceptor molecules located at the "outside" of the oligothiophene macrocycles. The complex formation leads to remarkably large Stern−Volmer constants of fluorescence quenching.

Results and Discussion

Materials. 2,4,7-trinitro-9-fluorenone was purchased from ACROS Chemicals. 2,4,5,7-Tetranitro-9-fluorenone was synthesized as described.[10] 4-Fluoro-3-trifluoromethylphenylboronic acid,[11] 6,6-dihydroxy-3,3,3′,3′-tetramethyl-spiro-1,1′-bisindane,[12] 5,5′-dibromo-2,2′-bithiophene (**1**), 5,5″-dibromo-2,2′,5′,2″-terthiophene (**2**),[13] 2,5-dibromo-3,4-(ethylenedioxy)thiophene (**3**),[14] and 3,4:3′,4′-bis(ethylenedioxy)-2,2′-bithiophene[15] were prepared according to the literature (Scheme 1). 5,5′-Dibromo-3,4:3′,4′-bis(ethylenedioxy)-2,2′-bithiophene (**4**) was prepared from 3,4:3′,4′-bis(ethylenedioxy)-2,2′-bithiophene by bromination with NBS.[7] 5,5′-Bis(4-fluoro-3-trifluoromethylphenyl)-2,2′-bithiophene (**5a**) and the macrocycle **6a** were synthesized as reported by Köhler et al.[8] The synthesis of the novel difluorooligoaryl monomers 5,5″-bis(4-fluoro-3-trifluoromethylphenyl)-2,2′:5′,2″-terthiophene (**5b**), 2,5-bis(4-fluoro-3-trifluoromethylphenyl)-3,4-ethylenedioxythiophene (**5c**), 5,5′-bis(4-fluoro-3-trifluoromethylphenyl)-3,4:3′,4′-bis(ethylenedioxy)-2,2′-bithiophene (**5d**), and the corresponding macrocycles **6b**, **6c**, and **6d** follows the procedure of Köhler et al.[8]

Molecular Structure. Köhler et al.[8] already analyzed the X-ray single-crystal structure of the crystalline macrocycle **6a** in its chiral form and reported that the individual diphenylbithiophene moieties were distinctly flattened to nearly planar. The mutual distortion between both diphenylbithiophene chro-

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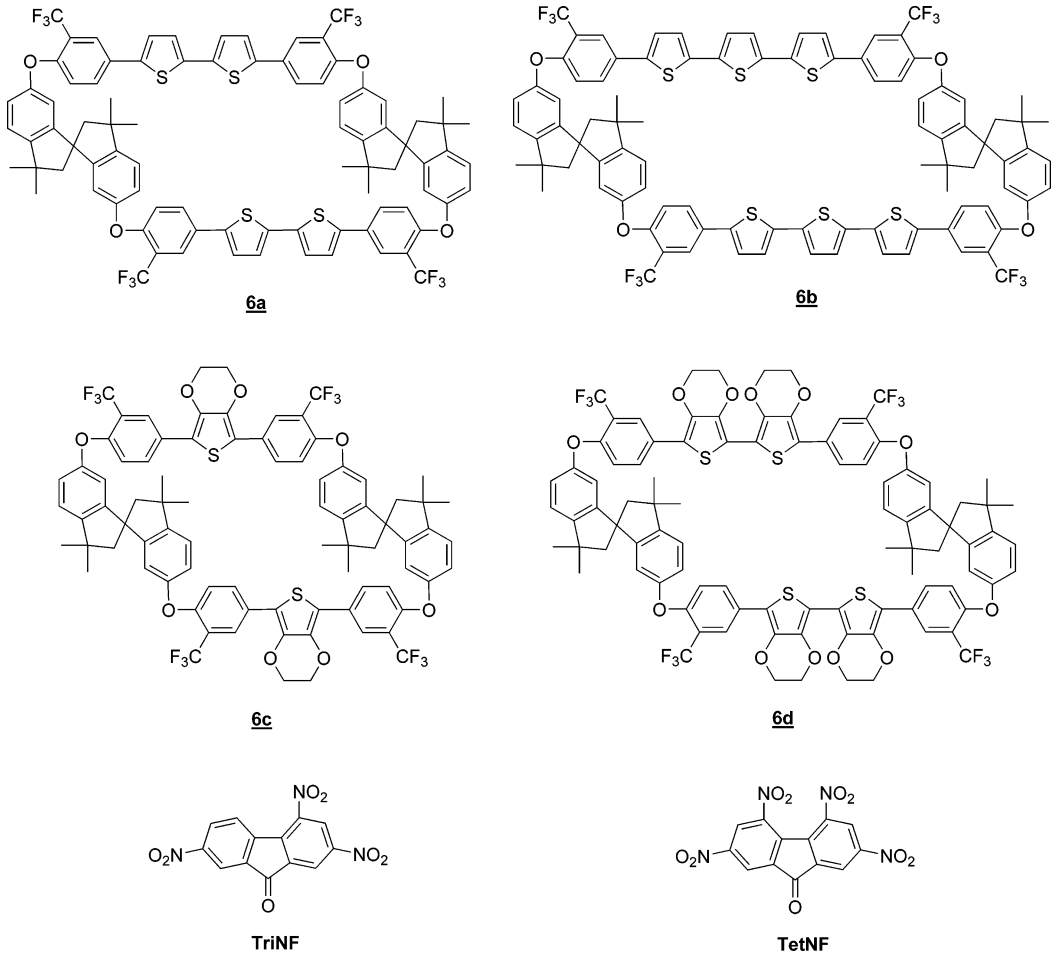


Figure 1. Structures of donor macrocycles and acceptors used in this study

TABLE 1: Absorption and Photoluminescence Data of the Macrocycles 6a−6d

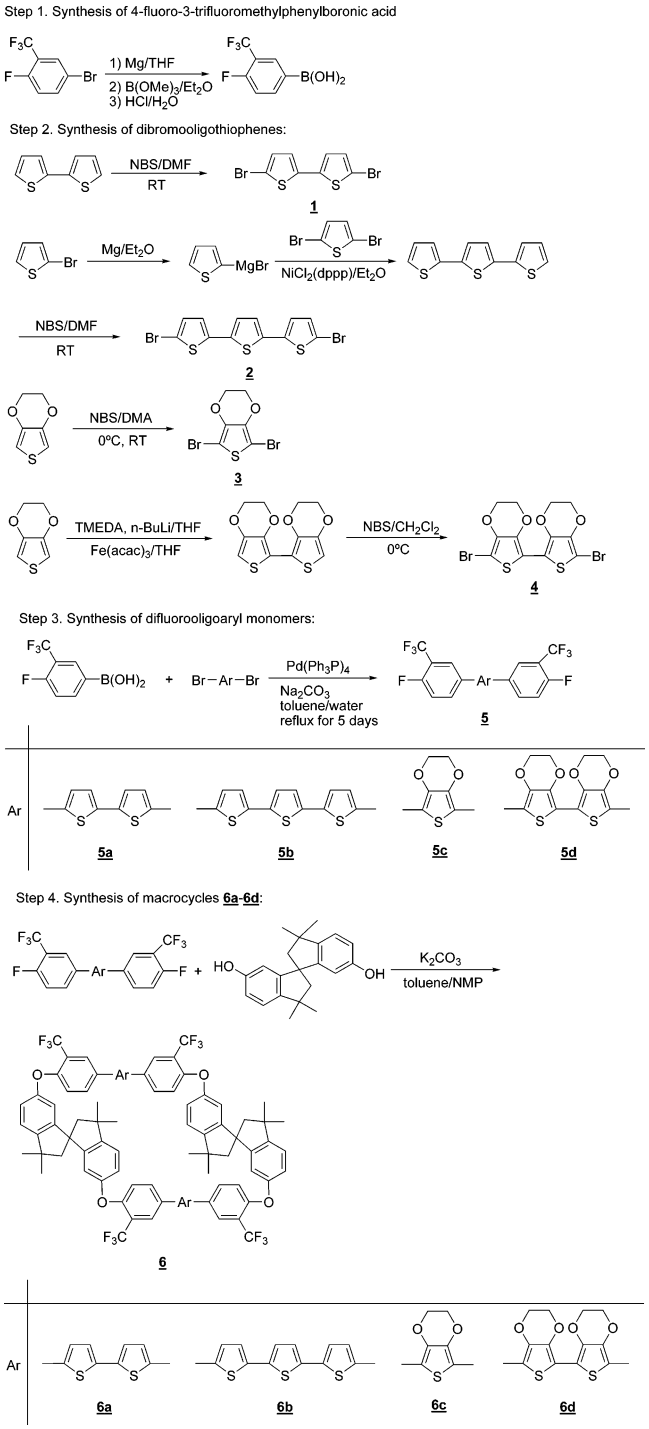
	6a	6b	6c	6d
absorption (λ_{abs})*	383 (423 sh)	414 (455 sh)	357 (378 sh)	406 (392 sh, 434)
fluorescence (λ_{em})*	473 (450, 510 sh)	520 (491, 555 sh)	425 (405 sh)	489 (461, 525)

mophores of the macrocycle was about 30°, the minimum distance between both diphenylbithiophenes about 3.65 Å (Figure 2). However, the crystals of the three novel macrocycles **6b**, **6c**, and **6d** were too thin to be analyzed by X-ray.

Because all macrocycles **6a**−**6d** are electron-rich compounds, we started complexation experiments with several electron-deficient acceptors. First, we tested a series of neutral (1,4-dinitrobenzene, 1,3,5-trinitrobenzene, 7,7,8,8-tetracyanoquinodimethane) and cationic electron acceptors (methyl, ethyl, and *n*-hexyl viologen). Unfortunately, ^{1}H NMR spectra of such donor/acceptor mixtures did not show any chemical shifts of characteristic signals, excluding the formation of donor/acceptor complexes. As a next step, we switched to tri- or tetranitro-9-fluorenone as electron-deficient partners with a more extended π-conjugated system. Now, donor/acceptor complexes are readily formed. Crystallization of the dark-colored mixtures in dichloromethane gave black crystalline solids with a 1:1 molar ratio of donor/acceptor. The X-ray structural analysis of a single crystal of {**6a**}·{TetNF} clearly showed that columnar π-stacked donor/acceptor complexes are formed with the stacks composed of alternating donor and acceptor molecules. The TetNF acceptor molecules are located at the "outside" of the oligothiophene macrocycles. Unfortunately, the single crystal of {**6a**}·{TetNF} was somewhat disordered and a full resolution of the crystal structure was not possible (R only 0.31). From these findings, it is concluded that chemical structure of the π-conjugated acceptor plays an important role in the interaction of macrocyclic donor and acceptor and in the formation of crystalline donor/acceptor complexes.

Absorption and Fluorescence Spectroscopy. Figure 3 shows the absorption (a) and emission (b) spectra of the macrocycles **6a**−**6d** dissolved in chloroform. Replacing the diphenylbithiophene chromophore of **6a** by the larger diphenylterthiophene chromophore of **6b** results in a 31 nm red-shift of the long wavelength absorption maximum λ_{max}. Replacing the diphenylbithiophene chromophore of **6a** by the more electron-rich diphenyl-bis-EDOT chromophore of **6d** results in a 23 nm red-shift of the absorption maximum. Macrocycles **6a**, **6b**, and **6c** only display a weak low-energy shoulder of the 0−0 transition (Table 1). Interestingly, the diphenyl-bis-EDOT based macrocycle **6d** shows a more pronounced vibronic resolution with a well-resolved 0−0 transition, indicating a fully planarized ground state of the diphenyl-bis-EDOT chromophore. The emission spectra of **6a**, **6b**, and **6d** display a pronounced vibronic structure of the photoluminescence emission. All macrocycles show very similar Stokes shifts of 1420−1610 cm^{-1} ($1/\lambda_{abs} - 1/\lambda_{em}$). The fully planarized structure of oligo-EDOT chromophores (as present in macrocycle **6d**) has been attributed to S···O intramolecular interactions between the

SCHEME 1: Reaction Schemes for Macrocycle Synthesis



EDOT units that support planarization and rigidification of the conjugated system, resulting in an enhanced-electron delocalization.[14]

The occurrence of dark-colored solutions and black crystalline precipitates upon mixing the yellow solution of the macrocycles **6a** or **6b** with the pale-yellow solution of 2,4,7-trinitro or 2,4,5,7-tetranitro-9-fluorenone is indicative for the formation of donor/acceptor complexes. UV−Vis spectra of dichloromethane solutions are shown in Figure 4. Part (a) compares the UV−vis spectra of **6a**, TriNF, and the black complex {**6a**}·{TriNF}. The spectrum of the complex (recorded at high concentration) shows a red-shift of the absorption edge of ca. 20 nm when compared with the absorption edge of the donor **6a**. However, well-resolved low-energy absorption bands of the complexes are not observed. Part (b) shows similar data for **6b**, TetNF, and the black complex {**6b**}·{TetNF}. The spectrum of the complex also shows a red-shifted absorption edge (ca. 24 nm) when compared with the absorption edge of **6b**. The red-shifted absorption edges indicate the occurrence of charge-transfer contribution in the optical spectra. Similar experiments to characterize donor/acceptor complexes have been described by other authors.[16]

NMR Analysis. To quantify the complex formation, ^{1}H NMR spectroscopy was often employed to determine binding constants of donor/acceptor complexes.[17] The NMR titration method means titration of a host (donor or acceptor) with increasing amounts of the corresponding guest and follows the change in the chemical shift of characteristic signals of the NMR spectrum. The values are calculated by subtracting the chemical shift of the mixture from that of the pure host.

Our ^{1}H NMR spectra of donor/acceptor complexes were recorded in 1,1,2,2-tetrachlorethane-d_2. The largest ^{1}H NMR shift was obtained for H-12 of **6a** (upfield shift) in the systems **6a** + TriNF and **6a** + TetNF, and for H-13 of **6b** (upfield shift) in the systems **6b** + TriNF and **6b** + TetNF. Figure 5 depicts the ^{1}H NMR shifts of the characteristic signals of the donor upon addition of increasing amounts of the acceptor. At a donor/acceptor ratio of 1:4, the shift of H-12 of **6a** is 0.0112 ppm for TetNF and 0.0096 ppm for TriNF as acceptors; the shift of H-13 of **6b** is 0.0173 ppm for TetNF and 0.0137 ppm for TriNF. These findings indicate a higher complex stability for complexes based on **6b** in comparison to **6a**. However, the ^{1}H NMR titration curves of Figure 5 did not show any signs of saturation even at high donor/acceptor ratios of 1:4. Therefore, the stoichiometry of the complexes in solution could not be calculated from these curves. Also, Job's method[18] failed. Unfortunately, we could not obtain sufficient NMR data for donor/acceptor complexes based on the macrocycles **6c** and **6d**. Also Balch et al.[16a] successfully isolated single crystals of {Au_3(MeN═COMe)$_3$}/{2,4,5,7-tetranitro-9-fluorenone} donor/acceptor complex, but the ^{1}H NMR spectra of the donor/acceptor mixtures in solution did not show significant ^{1}H NMR shifts.

The low ^{1}H NMR shifts values do not indicate the presence of inclusion complexes for which much higher shifts are expected, but the formation of donor/acceptor complexes with the acceptor molecules localized at the outside of the macrocycles.

Fluorescence Quenching Study. The formation of donor/acceptor complexes is accompanied by fluorescence quenching of the macrocycle emission. Corrected fluorescence emission spectra of **6c** upon addition of TriNF are shown in Figure 6a. As the concentration of TriNF increases, the emission intensity of **6c** is drastically reduced.

There are two general mechanisms of fluorescence quenching: (1) so-called static quenching via formation of a stable complex and (2) so-called dynamic quenching within a sphere-of-action.[19] The experimentally observed fluorescence quenching can be described by the so-called Stern−Volmer equation:

$$\frac{F^0}{F} = 1 + K_{sv}\,[\text{quencher}]$$

F^0 is the fluorescence intensity in the absence, and F is the fluorescence intensity in the presence of the quencher. At low quencher concentrations, F^0/F increases linearly with increasing quencher concentration for all complexes **6a**−**6d**. Fitting the data for low quencher concentrations ($c < 3 \times 10^{-5}$ M) with the linear Stern−Volmer equation results in the Stern−Volmer

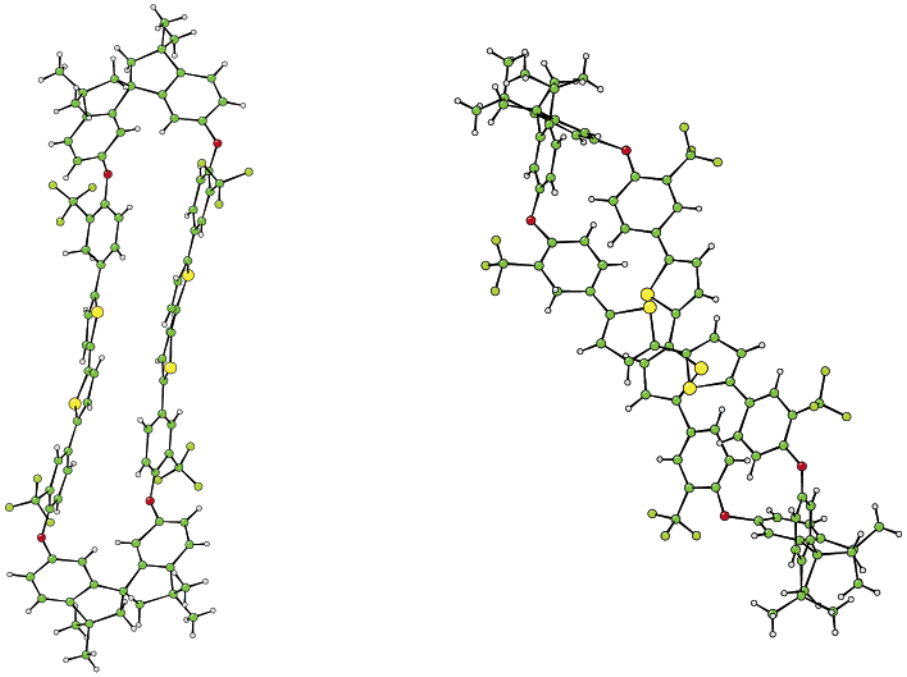


Figure 2. X-ray crystal structure of the macrocycle **6a** (reprinted after the literature ref 8).

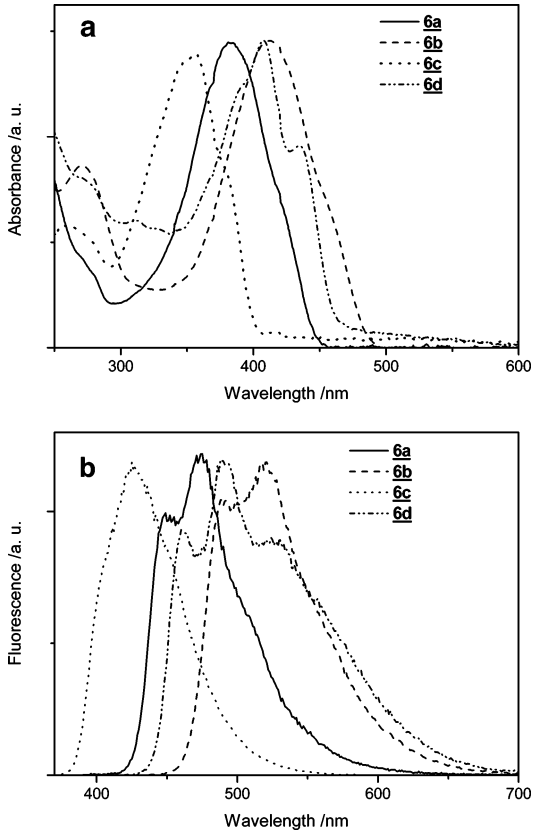


Figure 3. Normalized absorption (a) and emission (b) spectra of macrocycles **6a**−**6d** in dilute chloroform solution. The emission spectra are recorded by exciting at the long wavelength maximum of the absorption spectra.

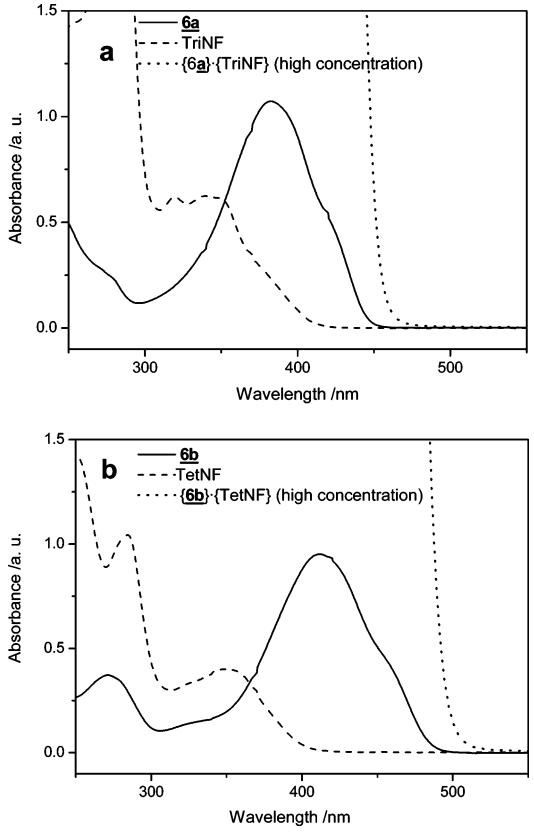


Figure 4. UV−Vis absorption data of donor/acceptor complexes: (a) dichloromethane solutions of **6a** (solid line), TriNF (dashed line), and the {**6a**}{TriNF} complex (high concentration, dotted line); (b) dichloromethane solutions of **6b** (solid line), TetNF (dashed line), and the {**6b**}{TetNF} complex (high concentration, dotted line).

constants K_{sv} listed in Table 2. In this concentration range, the fluorescence quenching is most pronounced for the diphenyl-EDOT macrocycle **6c**, with somewhat increased K_{sv} values for TetNF complexes (in relation to TriNF complexes). As the quencher concentration increases, the Stern−Volmer plots for the four macrocycles show a different behavior (Figure **6b**). The plots for two macrocylces **6a** and **6c** become clearly superlinear, in contrast to the curves for **6b** and **6d**. To explain such behavior, the concept of a sphere-of-action (dynamic quenching) was introduced by Frank and Vavilov.[20] These different quenching characteristics of the macrocycles **6a**−**6d** in our study have to be clarified in further experiments.

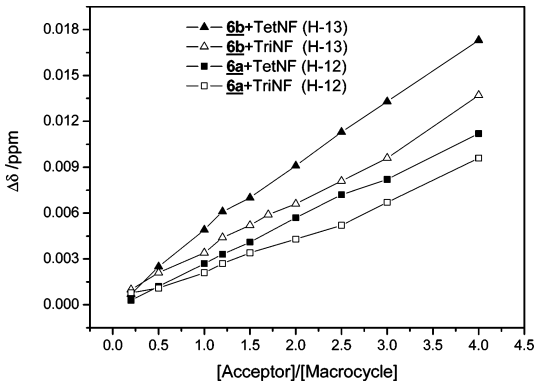


Figure 5. ^{1}H NMR titration curves with a macrocycle concentration of 1×10^{-3} M and increasing acceptor concentrations (0.2×10^{-3}, 0.5×10^{-3}, 1×10^{-3}, 1.2×10^{-3}, 1.5×10^{-3}, 2×10^{-3}, 2.5×10^{-3}, 3×10^{-3}, and 4×10^{-3} M) in 1,1,2,2-tetrachlorethane-d_2.

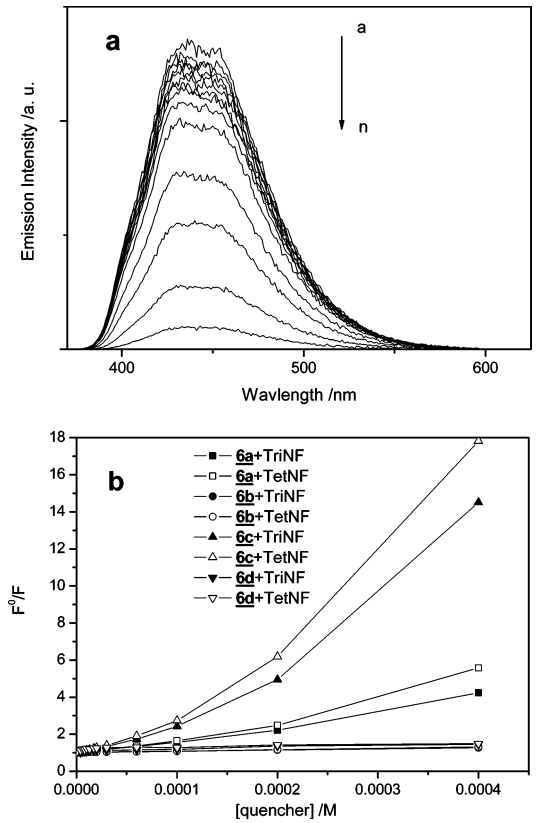


Figure 6. (a) Fluorescence emission spectra of **6c** (10 μM) in the presence of increasing TriNF concentration (a−n; 0, 2, 4, 6, 8, 10, 13, 17, 20, 30, 60, 100, 200, 400 μM). (b) Stern−Volmer plots for fluorescence quenching of **6a**, **6b**, **6c**, and **6d** (10 μM) at high TriNF and TetNF concentrations. The data were recorded in $CHCl_3/C_2H_2Cl_4$ (5:1, v/v).

TABLE 2: Photoluminescence Quenching of Macrocycles 6a−6d by TriNF and TetNF

	K_{sv} (M^{-1}) for donor			
acceptor	**6a**	**6b**	**6c**	**6d**
TriNF	5.8×10^3	1.6×10^3	1.1×10^4	6.8×10^3
TetNF	6.5×10^3	1.7×10^3	1.3×10^4	7.5×10^3

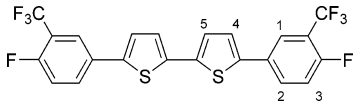
Conclusion

In summary, four rigid electron-rich macrocycles **6a−6d** have been synthesized and characterized by optical spectroscopy and ^{1}H NMR analysis.[21] They form donor/acceptor complexes with tri- or tetranitro-9-fluorenone. Three crystalline complexes with a 1:1 donor/acceptor ratio have been isolated with relatively weak ^{1}H NMR shifts of characteristic signals in dissolved donor/acceptor mixtures. Because of X-ray structure analysis, the π-stacked, columnar donor/acceptor complexes are not inclusion compounds, but columnar stacks composed of alternating donor and acceptor molecules. The complex formation is accompanied by remarkably large Stern−Volmer constants of fluorescence quenching of up to 1.3×10^4 M^{-1} for **6c**/TetNF system.

Experimental Section

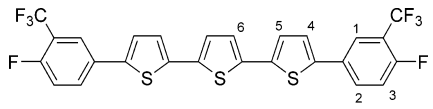
General Consideration. All reactions were carried under an argon atmosphere. The solvents were used as commercial p.a. quality. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker ARX 400 spectrometer. UV−Vis and fluorescence spectra were recorded on a Jasco V-550 UV−Vis and a VARIAN fluorescence spectrophotometer, respectively. Mass spectra were measured with a Zab 2SE FPD mass spectrometer.

Synthesis of the Difluorooligoaryl Monomers *5b, 5c,* and *5d.* 4-Fluoro-3-trifluoromethylphenylboronic acid (6.0 g, 28.8 mmol) and the dibromooligoaryl compound (12.0 mmol, 5,5″-dibromo-2,2′,5′,2″-terthiophene (**2**), 4.87 g; 2,5-dibromo-3,4-(ethylenedioxy)thiophene (**3**), 3.6 g; or 5,5′-dibromo-3,4:3′,4′-bis(ethylenedioxy)-2,2′-bithiophene (**4**), 5.28 g), toluene (90 mL), aqueous Na_2CO_3 solution (90 mL, 1 M), and $Pd(Ph_3P)_4$ (0.416 g, 3 mol %) were intensely stirred and refluxed for 5 days under argon. The organic layer was separated and the aqueous phase twice extracted with toluene (2×100 mL). The combined organic layers were washed with water (2×100 mL), dried ($MgSO_4$), and concentrated. The concentrated organic layer was filtered by column chromatography on silica gel with toluene/petroleum ether (10:1) as eluent. The compounds were further purified by recrystallization from a 1:1 mixture of toluene/hexane.



5a

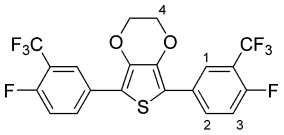
Yield: 56%. MS: *m/z*: 489 (M^+). Anal. Calcd for $C_{22}H_{10}F_8S_2$ (490.44 g/mol) (%): C, 53.87; H, 2.06; S, 13.07. Found: C, 53.97; H, 1.95; S, 13.87. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.71 (d, $J = 6.54$ Hz, 2H, H1); 7.68 (m, $J = 15.40$ Hz, 2H, H2); 7.19 (d, $J = 9.52$ Hz, 2H, H3); 7.17 (d, $J = 5.27$ Hz, 2H, H4); 7.14 (d, $J = 3.83$ Hz, 2H, H5). ^{13}C NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 157.92 (s); 140.74 (s); 137.47 (s); 131.21 (d); 130.83 (d); 125.43 (s); 125.40 (s); 124.43 (d); 124.02 (s); 119.02 (q); 118.05 (d). ^{19}F NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): −61.50 (d); −116.00 (m).



5b

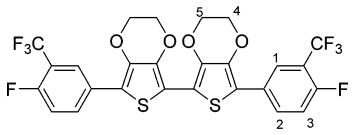
Yield: 50%. MS: *m/z*: 571 (M^+). Anal. Calcd for $C_{26}H_{12}F_8S_3$ (572.56 g/mol) (%): C, 54.54; H, 2.12. Found: C, 54.04; H, 2.09. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.71 (d, $J = 8.34$ Hz, 2H, H1); 7.67 (m, $J = 15.25$ Hz, 2H, H2); 7.17 (d, $J = 2.11$ Hz, 2H, H3); 7.16 (d, $J = 3.06$ Hz, 2H, H4); 7.11 (d, $J = 3.75$ Hz, 2H, H5); 7.08 (s, 2H, H6). ^{13}C NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 157.88 (s); 140.56 (s); 137.54 (s); 136.28 (s); 131.16 (d); 130.85 (d); 125.39 (s); 125.25 (s); 125.15 (s);

124.37 (d); 124.01 (s); 119.04 (q); 118.02 (d). ^{19}F NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): −61.49 (d); −116.05 (m).



5c

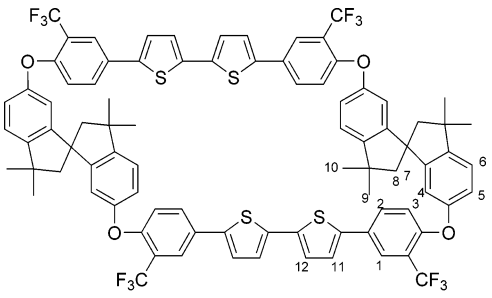
Yield: 41%. *m*/*z*: 466 (M) and 465 (M^+). Anal. Calcd for $C_{20}H_{10}O_2F_8S$ (466.36 g/mol) (%): C, 51.51; H, 2.17; S, 6.87. Found: C, 52.24; H, 2.24; S, 6.59. ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm): 8.04 (d, J = 8.67 Hz, 2H, H1); 7.97 (m, J = 15.60 Hz, 2H, H2); 7.41 (t, J = 19.26 Hz, 2H, H3); 4.50 (s, 4H, H4). ^{13}C NMR (400 MHz, acetone-d_6) δ (ppm): 160.80 (s); 158.28 (s); 141.46 (s); 133.10 (d); 131.25 (d); 125.60 (dd); 123.01 (s); 119.43 (d); 114.36 (s); 66.50 (s). ^{19}F NMR (400 MHz, acetone-d_6) δ (ppm): −62.49 (d); −119.09 (m).



5d

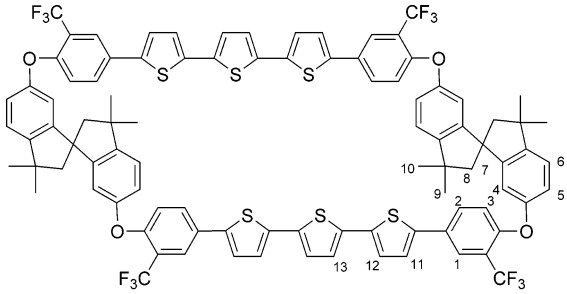
Yield: 15%. *m*/*z*: 606 (M^+). Anal. Calcd for $C_{26}H_{14}O_4F_8S_2$ (606.52 g/mol) (%): C, 51.48; H, 2.33; S, 10.57. Found: C, 51.10; H, 2.47; S, 10.16. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.89 (d, J = 6.45 Hz, 2H, H1); 7.82 (m, J = 12.86 Hz, 2H, H2); 7.13 (t, J = 18.85 Hz, 2H, H3); 4.36 (m, J = 4.69 Hz, 4H, H4); 4.32 (m, J = 4.18 Hz, 4H, H5). ^{13}C NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 156.82 (s); 138.79 (s); 138.08 (s); 131.24 (d); 130.04 (d); 124.46 (d); 123.90 (s); 119.16 (s); 117.51 (d); 112.90 (s); 109.04 (s); 65.22 (s). ^{19}F NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): −61.30 (d); −117.73 (m).

Synthesis of the Macrocycles 6b, 6c, and 6d. 6,6′-Dihydroxy-3,3,3′,3′-tetramethyl-spiro-1,1′-bisindane (3 mmol), difluorooligoaryl monomer (1 mmol; 5,5″-bis(4-fluoro-3-trifluoromethylphenyl)-2,2′:5′,2″-terthiophene (**5b**), 0.57 g; 2,5-bis(4-fluoro-3-trifluoromethylphenyl)-3,4-ethylenedioxythiophene (**5c**), 0.47 g; or 5,5′-bis(4-fluoro-3-trifluoromethylphenyl)-3,4:3′,4′-bis(ethylenedioxy)-2,2′-bithiophene (**5d**), 0.61 g) and K_2CO_3 (2.2 mmol) were placed in a flask equipped with a Dean−Stark trap. Toluene (60 mL) and 1-methyl-2-pyrrolidone (NMP; 30 mL) were added. The mixture was refluxed under argon for 5 h to remove all water. Afterward, the mixture was heated for another 8 h at 200 °C. After removal of solvent, the product was poured into methanol/aqueous HCl. The precipitate was filtered and washed several times with hot water. The macrocycle was purified by column chromatography on silica gel, with the eluents described in the following paragraphs.



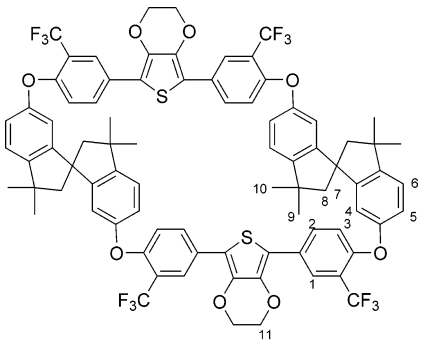
6a

After chromatography on silica gel with hexane/toluene (9:1) as eluent, the yellow macrocycle was recrystallized from THF. Yield: 20%. FD-MS: *m*/*z*: 1517.6 (M^+). Anal. Calcd for $C_{86}H_{64}O_4F_{12}S_4$ (1517.74 g/mol) (%): C, 68.05; H, 4.26; S, 8.45. Found: C, 68.15; H, 4.15; S, 9.20. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.71 (s, J = 1.98 Hz, 4H, H1); 7.14 (d, J = 8.20 Hz, 4H, H6); 7.04 (dd, J = 10.79 Hz, 4H, H2); 6.84 (dd, J = 10.45 Hz, 4H, H5); 6.82 (d, J = 3.81 Hz, 4H, H11); 6.71 (d, J = 3.81 Hz, 4H, H12); 6.58 (s, J = 2.25 Hz, 4H, H4); 6.37 (d, J = 8.72 Hz, 4H, H3); 2.40 (d, J = 13.28 Hz, 4H, H8); 2.26 (d, J = 13.16 Hz, 4H, H7); 1.37 (s, 12H, H9); 1.31 (s, 12H, H10). ^{13}C NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 156.66 (s); 154.36 (s); 153.27 (s); 150.01 (s); 140.53 (s); 136.94 (s); 130.04 (s); 127.75 (s); 124.71 (s); 124.05 (s); 123.80 (m); 122.28 (s); 120.70 (s); 119.80 (s); 117.51 (s); 116.90 (s); 114.30 (s); 59.21 (s); 57.54 (s); 43.76 (s); 32.12 (s); 30.05 (s). ^{19}F NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): −62.00 (s).



6b

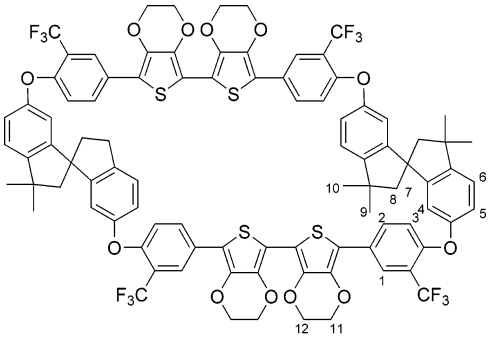
After chromatography on silica gel with hexane/toluene (4:1) as eluent, the yellow macrocycle was purified by recrystallization from THF. Yield: 18%. FD-MS: *m*/*z*: 1683.1 (M^+). Anal. Calcd for $C_{94}H_{68}O_4F_{12}S_6$ (1681.98 g/mol) (%): C, 67.12; H, 4.08; S, 11.44. Found: C, 67.55; H, 4.39; S, 11.05. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.71 (s, J = 1.86 Hz, 4H, H1); 7.14 (d, J = 8.20 Hz, 4H, H6); 7.08 (dd, J = 10.73 Hz, 4H, H2); 6.84 (dd, J = 10.34 Hz, 4H, H5); 6.77 (d, 4H, H11); 6.75 (s, 4H, H12); 6.74 (s, 4H, H13); 6.59 (s, J = 2.16 Hz, 4H, H4); 6.41 (d, J = 8.71 Hz, 4H, H3); 2.40 (d, J = 13.20 Hz, 4H, H7); 2.26 (d, J = 13,19 Hz, 4H, H8); 1.37 (s, 12H, H9); 1.31 (s, 12H, H10). ^{13}C NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 156.58 (s); 154.45 (s); 153.25 (s); 149.93 (s); 140.28 (s); 136.97 (s); 136.10 (s); 129.78 (s); 128.13 (s); 127.82 (s); 124.64 (s); 124.35 (s); 123.98 (m); 122.26 (s); 120.58 (s); 119.93 (s); 117.39 (s); 117.03 (s); 114.23 (s); 59.21 (s); 57.54 (s); 43.75 (s); 32.13 (s); 30.06 (s). ^{19}F NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): −61.97 (s).



6c

After chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent, the white macrocycle was purified by recrystallization from THF. Yield: 10%. FD-MS: *m*/*z*: 1470.1 (M^+).

Anal. Calcd for $C_{82}H_{64}O_8F_{12}S_2$ (1469.58 g/mol) (%): C, 67.01; H, 4.40. Found: C, 67.34; H, 4.30. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.78 (s, 4H, H1); 7.13 (d, J = 8.20 Hz, 4H, H6); 7.08 (d, J = 8.67 Hz, 4H, H2); 6.82 (dd, J = 10.39 Hz, 4H, H5); 6.55 (s, J = 2.14 Hz, 4H, H4); 6.17 (d, J = 8.85 Hz, 4H, H3); 4.14 (s, 8H, H11); 2.42 (d, J = 13.15 Hz, 4H, H7); 2.22 (d, J = 12.62 Hz, 4H, H8); 1.36 (s, 12H, H9); 1.33 (s, 12H, H10). ^{13}C NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 155.74 (s); 154.13 (s); 153.28 (s); 150.12 (s); 138.34 (s); 130.37 (s); 126.45 (s); 123.85 (s); 123.73 (s); 122.40 (s); 120.92 (s); 118.90 (m); 118.00 (s); 116.24 (s); 113.45 (s); 64.44 (s); 58.86 (s); 57.42 (s); 43.74 (s); 31.96 (s); 29.86 (s). ^{19}F NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): −61.86 (s).



6d

After chromatography on silica gel with hexane/toluene (1:1) as eluent, the yellow macrocycle was purified by recrystallization from THF. Yield: 8%. FD-MS: *m/z*: 1751 (M^+). Anal. Calcd for $C_{94}H_{72}O_{12}F_{12}S_4$ (1749.9 g/mol) (%): C, 64.51; H, 4.16; S, 7.33. Found: C, 64.57; H, 4.36; S, 7.48. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.81 (s, 4H, H1); 7.25 (d, J = 8.46 Hz, 4H, H6); 7.15 (d, J = 8.04 Hz, 4H, H2); 6.85 (d, J = 7.93 Hz, 4H, H5); 6.60 (s, 4H, H4); 6.24 (d, J = 8.87 Hz, 4H, H3); 4.27 (s, 8H, H11); 4.15 (s, 8H, H12); 2.44 (d, J = 13.41 Hz, 4H, H7); 2.30 (d, J = 13.10 Hz, 4H, H8); 1.40 (s, 12H, H9); 1.36 (s, 12H, H10). ^{13}C NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 155.69 (s); 154.68 (s); 153.41 (s); 150.02 (s); 137.95 (s); 134.06 (s); 131.00 (s); 130.69 (s); 129.07 (s); 127.52 (s); 123.86 (s); 121.26 (s); 118.10 (m); 116.51 (s); 113.32 (s); 109.21 (s); 105.75 (s); 64.78 (s); 60.57 (s); 57.30 (s); 43.72 (s); 31.90 (s); 29.99 (s). ^{19}F NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): −61.43 (s).

Synthesis of Donor/Acceptor Complexes. Black crystalline charge-transfer adducts of the macrocycles with tri- or tetranitro-9-fluorenone were obtained by mixing the components as dichloromethane solutions and storing a concentrated solution of the mixture in the refrigerator. The stoichiometry of the crystalline complexes was analyzed by elemental analysis and integration of the ^{1}H NMR spectra. Several attempts to isolate crystalline complexes have been made, but only the three successful attempts are documented here.

{***6a***}·{*TriNF*}. A pale-yellow solution of 2,4,7-trinitro-9-fluorenone (0.02 mmol) in 3 mL of dichloromethane was added to the yellow solution of the macrocycle **6a** (15.18 mg, 0.01 mmol) in 10 mL of dichloromethane. After shaking for a few minutes, the solution was filtered and the filtrate concentrated. The concentrated solution was dark brown in color and allowed to stand for several days in the refrigerator. Black crystals of the product gradually precipitated. The product was collected and dried. Anal. Calcd for the 1:1 adduct $C_{99}H_{69}O_{11}F_{12}S_4N_3$ (1832.95 g/mol) (%): C, 64.87; H, 3.80; N, 2.29; S, 6.99. Found: C, 64.73; H, 3.97; N, 2.38; S, 6.45. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 8.92 (d, 1H); 8.72 (d, 1H); 8.58 (d, 1H); 8.48 (dd, 1H); 8.26 (d, 1H); 7.71 (s, 4H); 7.14 (d, 4H); 7.04 (dd, 4H); 6.85 (dd, 4H); 6.81 (d, 4H); 6.70 (d, 4H); 6.59 (s, 4H); 6.37 (d, 4H); 2.41 (d, 4H); 2.26 (d, 4H); 1.37 (s, 12H); 1.31 (s, 12H).

{***6b***}·{*TriNF*}. A pale-yellow solution of 2,4,7-trinitro-9-fluorenone (0.02 mmol) in 3 mL of dichloromethane was added to the yellow solution of the macrocycle **6b** (16.82 mg, 0.01 mmol) in 10 mL of dichloromethane. After shaking for a few minutes, the solution was filtered and the filtrate concentrated. The concentrated solution was dark brown in color and allowed to stand for several days in the refrigerator. Black needles of the product gradually precipitated. The needles were collected and dried. Anal. Calcd for the 1:1 adduct $C_{107}H_{73}O_{11}F_{12}S_6N_3$ (1997.19 g/mol) (%): C, 64.34; H, 3.69; N, 2.10; S, 9.63. Found: C, 63.84; H, 3.74; N, 2.40; S, 9.48. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 8.93 (d, 1H); 8.73 (d, 1H); 8.58 (d, 1H); 8.48 (dd, 1H); 8.26 (d, 1H); 7.71 (s, 4H); 7.13 (d, 4H); 7.08 (dd, 4H); 6.84 (dd, 4H); 6.77 (d, 4H); 6.75 (s, 4H); 6.74 (s, 4H); 6.59 (s, 4H); 6.41 (d, 4H); 2.40 (d, 4H); 2.26 (d, 4H); 1.37 (s, 12H); 1.31 (s, 12H).

{***6b***}·{*TetNF*}. A pale-yellow solution of 2,4,5,7-tetranitro-9-fluorenone (0.02 mmol) in 3 mL of dichloromethane was added to the yellow solution of the macrocycle **6b** (16.82 mg, 0.01 mmol) in 10 mL of dichloromethane. After shaking for a few minutes, the solution was filtered and the filtrate concentrated. The concentrated solution was dark brown in color and allowed to stand for several days in the refrigerator. A black product gradually precipitated. The solid was collected and dried. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 8.91 (d, 2H); 8.79 (d, 2H); 7.71 (s, 4H); 7.14 (d, 4H); 7.08 (dd, 4H); 6.85 (dd, 4H); 6.77 (d, 4H); 6.74 (s, 4H); 6.73 (s, 4H); 6.59 (s, 4H); 6.41 (d, 4H); 2.40 (d, 4H); 2.26 (d, 4H); 1.38 (s, 12H); 1.31 (s, 12H).

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