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Synthesis and characterization of new trinitrofluorene-fullerene dyads as photosensitizers in photorefractive polymer materials. **Redox behavior and charge-transfer properties**

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Abstract—Novel trinitrofluorene– C_{60} dyads bearing a flexible polyether chain have been synthesized and characterized. UV–vis spectroscopy and cyclic voltammetric results indicate that there is no interaction in their ground states. NMR and electrochemical studies of dyads 2 and 3 in solution indicate the existence of a charge-transfer complex between the trinitrofluorene moieties and N-ethylcarbazol. Preliminary results of the photorefractive performance of these compounds as sensitizers in polymer composites based on poly(N-vinylcarbazole) are similar to that of C₆₀, but with shorter response times and slightly lower gain coefficients. © 2006 Elsevier Ltd. All rights reserved.

1. Introduction

The photorefractive (PR) effect can be defined as a spatial modulation of the index of refraction induced by a light intensity pattern.¹ In order to display this effect, the material must show both photoconductivity and a high nonlinear response and/or birefringence. Under these conditions, an internal redistribution of charges takes place, which induces the variation on the refraction index. This effect was first observed in 1966 in an inorganic crystal of LiNbO₃.² To name a few, other examples of inorganic materials in which the PR effect has been examined are BaTiO₃, KNbO₃, Bi₁₂SiO₂₀ (BSO), GaAs.³ The applications of these materials have been limited by the difficulty in crystal growing and sample preparation. Organic PR materials, however, exhibit refractive index modulations and gain coefficients which are superior compared to their inorganic counterparts, and due to their versatility, lower cost and easier fabrication and processability are becoming promising candidates for applications in optical holographic data storage, real-time image processing, and phase conjugation.4

The PR effect was observed for the first time in organic crystals in 1990 by Sutter and Günter.⁵ Just one year later, in 1991, Ducharme et al. demonstrated PR effect in a polymeric composite.⁶ Since then, several research groups have focused experimental efforts on the development of PR polymers.⁷

The physical phenomena necessary to achieve photorefractivity are photoinduced charge generation, charge transport, trapping, and electrooptical nonlinearity. One of the major approximations to achieve PR effect in organic materials, and the most widely spread indeed, is the use of functional polymers (which are responsible of one or two of the functional properties needed to originate PR effect) doped with molecules responsible for the rest of the functional properties.⁸ The use of polymeric compositions has led to materials with high gain coefficients $(\hat{\Gamma})$, in the order of 200 cm⁻¹, and with diffraction efficiencies (η) of 100%.⁹ However, the most important drawback of organic polymers is the low speed of grating formation, that is, the high response time (τ) , although some compositions are described having speeds in the range of 10 ms. Research has been focused in the design of improved nonlinear optical chromophores,¹⁰ in order to increase Γ while maintaining high values of η , but little effort has been paid to increase the photorefractive speed. Moerner and Twieg demonstrated that, at least in certain cases, speed is limited by photoconductivity (σ_{ph}) rather than by chromophore orientation.¹¹ Due to the fact that photoconductivity

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depends on charge generation efficiency, the improvement of the latter should enhance the performance of the material. This leads to the need of a better photosensitizer.

Charge photogeneration efficiency is governed by a competition between recombination of a charge carrier with its parent countercharge, termed geminate recombination, and electron-hole pair dissociation.¹² In order to favor the second possibility, a fast electron transfer from another molecule must take place, that is, an adequate relationship between HOMO and LUMO orbitals of photosensitizer and charge transporting molecule must be achieved. The best performance is obtained by optimizing the charge-transfer (CT) properties between a given sensitizer (an acceptor-like molecule or moiety) and its parent transport molecule (a donor-like molecule or moiety). To date, the most successful class of sensitizers incorporated into photoconductor polymers have been C_{60} and 2,4,7-trinitro-9-fluorenone (TNF).

 C_{60} is a unique molecule with a vast array of interesting properties. Among them, it is an outstanding photosensitizer due to its long-lived triplet state, high absorption, the presence of various stable oxidation states and the low degree of charge recombination.¹³ It has been found that the photogeneration efficiency of poly(*N*-vinylcarbazole) (PVK) based composites sensitized with C₆₀ is higher than when other sensitizers are used.¹⁴ On the other hand, the synthesis of functionalized C₆₀ is becoming more and more interesting due to their remarkable optoelectronic properties.¹⁵ C₆₀ derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester ([6,6]-PCBM) has been used as photosensitizer in different photoconducting polymer-based composites presenting a poor charge-carrier generation efficiency.¹⁶

On the other hand, TNF is a strong electron acceptor, even better than C_{60} , a characteristic which allows the formation of robust CT complexes with charge transporting molecules of the carbazol series.¹⁷ Thus, the covalent linking of C_{60} and trinitrofluorenone would render a photosensitizer combining the exceptional properties of each moiety, and is expected to optimize the charge-transfer properties with PVK increasing the charge generation efficiency.

Another point of interest related to the photosensitizer is the laser wavelength needed for the photoexcitation. The election depends on the absorption profiles of the photosensitizer and the nonlinear chromophore. In fact, absorption due to the chromophore should be avoided to reduce losses, while the photosensitizer should show enough absorption to allow charge generation, but not enough to minimize losses. Therefore, photosensitizers in the near infrared domain are interesting. Moreover, sensitizing in this region allows to use commercially-available, cheap lasers, which is a major consideration if these materials are to be used in technologically useful devices. While C_{60} and TNF are irradiated at 633 nm, 2,4,7-trinitro-9-dicyanomethylen-fluorene (TNDCF)^{18–20} operates at 830 nm. [6,6]-PCBM was also utilized as a near infrared photosensitizer in photorefractive polymer composites.²¹

With all these considerations in mind, we decided to synthesize dyads containing C_{60} and TNF moieties

covalently linked in order to benefit of a synergic collaboration between them. Thus, C_{60} -TNF dyads **1a**-c were synthesized in which the distance between the two subunits was regulated by the position of the phenyl substitution from *ortho* to *meta* to *para*. The photorefractive properties of their compositions with PVK and 4-piper-idindicyanostyrene (PDCST) were determined and compared with those of the corresponding compositions bearing C_{60} . While the composite with C_{60} showed a slightly higher gain coefficient, the compositions with **1a**-c, proved to be 2–3 times faster in grating formation, that is, they had a response time 2–3 times lower when high electric fields were applied.²²



This very positive result prompted us to redesign our photosensitizers. Here we present the synthesis, characterization and electrochemical study of dyads 2 and 3 bearing a flexible polyether chain to enhance the solubility in organic solvents, to avoid phase segregation, to allow a better interaction between the moieties, to introduce the possibility of ion complexation, and prepared to work in the near infrared region.



2. Results and discussion

2.1. Synthesis of 2,5,7-trinitrofluorenone– C_{60} (TNF– C_{60}) and 2,5,7-trinitro-9-dicyanomethylenfluorene– C_{60} (TNDCF– C_{60}) dyads

The hydroxyformyl derivative **4** was prepared by esterification of 4-formylbenzoic acid with tetraethylene glycol using *N*,*N*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP). The reaction of **4** with 2,5,7-trinitrofluorenone-4-carboxylic acid chloride $(\mathbf{5})^{23}$ in CH₂Cl₂ in the presence of DMAP and triethylamine afforded the corresponding trinitrofluorenone derivative **6**.

Finally, the synthesis of C_{60} -TNF derivative **2** was accomplished by Prato's reaction²⁴ from aldehyde **6** with sarcosine and C_{60} (Scheme 1).



Scheme 1.

The synthesis of the 2,5,7-trinitro-9-dicyanomethylenfluorene– C_{60} dyad **3** was envisaged by two different vias (Scheme 2): (a) Knoevenagel reaction of TNF– C_{60} derivative **2** and malononitrile, and (b) Prato reaction between the trinitrodicyanomethylenfluorene aldehyde derivative **7**, sarcosine and C_{60} . Thus, reaction of TNF– C_{60} derivative **2** with an excess of malononitrile in DMF at room temperature over a long duration afforded the adduct TNDCF– C_{60} **3** in a good (64%) yield.





The synthesis of 2,5,7-trinitro-9-dicyanomethylenfluorene-4-carboxylic acid chloride (9) from 2,5,7-trinitro-9-dicyanomethylenfluorene-4-carboxylic acid (8) and SOCl₂, followed by the condensation with the hydroxyaldehyde 4 to obtain the formyldicyanomethylenfluorene derivative 7 in a one pot reaction (Scheme 2), gave rise to a mixture of aldehydes 6 and 7 difficult to separate by column chromatography. This hydrolysis of the dicyanomethylenefluorene aldehyde 7 to the fluorenone aldehyde 6 could be attributed to the presence of acidic conditions while generating the acid chloride derivative.

For comparison purposes, methyl 2,5,7-trinitrofluorenone-4carboxylate (**10**, MTNFC) and methyl 2,5,7-trinitrodicyanomethylenfluorene-4-carboxylate (**11**, MTNDCM) were prepared in a good yield from 2,5,7-trinitrofluorenone-4-carboxylic acid in methanol using DCC and DMAP, following a modification of a previously reported procedure (Scheme 3).



Scheme 3.

The new dyads TNF– C_{60} were fully characterized by ¹H, ¹³C NMR, MALDI-TOF mass spectrometry and elemental analysis.

2.2. Spectroscopic studies

Figure 1 shows the UV–vis spectra of 2 and 3, together with that of C_{60} for comparison in toluene. The UV–vis spectra of 2 and 3 display strong absorptions due to both the TNF and the fullerene moieties. Both compounds show a typical 1,2-methanofullerene UV–vis spectrum, with a sharp absorption at 430 nm and a broader band at around 700 nm^{24b} showing



Figure 1. UV–vis spectra of compounds TNF–C₆₀ 2 and TNDCF–C₆₀ 3 (solid line) and C₆₀ (dotted line) in toluene as solvent.

that both the TNF and the C_{60} moieties have little or no electronic influence on each other in the ground state. It is noteworthy that compound **3** has a stronger absorption in the near IR than compound **2**, because as a consequence, the former could have application as near infrared photosensitizer.

In the presence of an excess of alkaline metal cations (Na⁺, K⁺ and Rb⁺) the UV-vis spectra of dyads **2** and **3** do not show any shift in the absorption bands. A similar result was observed in ¹H NMR. Both observations suggest the absence of a ground state interaction between the two chromophores although the complex was formed.

We also studied the ability of the TNF– C_{60} dyads 2 and 3 to form intermolecular CT complexes with donors in solution using *N*-ethylcarbazole (ECZ) as the π -donor. The appearance of additional bands in the visible region was not detected maybe due to the overlapping with the signals corresponding to the C_{60} derivative. However, addition of different amounts of ECZ to a solution of dyads 2 and 3 in CDCl₃ produced pronounced changes both in chemical shifts and splitting patterns for protons within the fluorene ring moiety as observed by ¹H NMR (Figs. 2 and 3).



Figure 2. ¹H NMR spectra (CDCl₃, 500 MHz, 298 K) of the TNF-C₆₀ dyad 2 (A), a 1:1 mixture of 2:ECZ (B), a 1:10 mixture of 2:ECZ (C), a 1:30 mixture of 2:ECZ (D) and a 1:70 mixture of 2:ECZ (E).

Upon addition of the same excess of ECZ larger chemical shifts were observed for the aromatic fluorene protons in compound **3** than in compound **2**. For example, addition of 70 equiv of ECZ give rise to a $\Delta\delta H^8 = 1.03$ ppm for TNDCF-C₆₀ dyad **3** and to a $\Delta\delta H^8 = 0.36$ ppm for TNF-C₆₀ dyad **2**. These observations agree with the higher electron withdrawing character of the TNDCF moiety versus the TNF, leading to a better interaction with ECZ.

Interestingly, no change could be detected by 1 H NMR in the signals corresponding to the fulleropyrrolidine moiety in both dyads 2 and 3 upon addition of ECZ, even to a 100-fold



Figure 3. ¹H NMR spectra (CDCl₃, 500 MHz, 298 K) of the TNDCF– C_{60} dyad **3** (A), a 1:1 mixture of **3**:ECZ (B), a 1:10 mixture of **3**:ECZ (C), a 1:30 mixture of **3**:ECZ (D) and a 1:70 mixture of **3**:ECZ (E).

excess. This result is attributable either to an interaction of the ECZ with another fragment of the ball or to the absence of any interaction at all between ECZ and the ball. To provide insight into this question, we performed ¹³C NMR in $CDCl_3$ at room temperature of dyads 2 and 3 each in the presence of a 100-fold excess of ECZ. As already pointed out for ¹H NMR, a dramatic effect on the chemical shifts of the signals corresponding to the fluorene moieties was observed ($\Delta \delta \approx 1.5$ and $\Delta \delta \approx 4$ ppm for complexes 2:ECZ and 3:ECZ, respectively), while only minor changes could be detected in the signals corresponding to the fulleropyrrolidine moiety ($\Delta \delta \approx 0.4$ ppm). For the rest of atoms of the ball, the displacement was so small, if any, that the close proximity of such a number of signals precluded any assignation. Thus, it seems that the ECZ interacts only with the fluorene moiety.

The association constants of the TNF– C_{60} :ECZ and TNDCF– C_{60} :ECZ complexes were determined at room temperature from the dependence of the δH^8_{obs} on the



Figure 4. Plot of δ_{obs} H⁸ of compound **3** as a function of the concentration of *N*-ethylcarbazole, where $[3]_0=0.83\times10^{-3}$ M. Iterative fitting (solid line) affords $\Delta\delta_{max}=1.73$ and the association constant $K_a=21.3\pm0.6$ M⁻¹.

concentration of ECZ at a constant concentration of 10^{-3} M of dyads 2 and 3 by the use of an iterative nonlinear regression analysis (Fig. 4). The maximum complexation-induced shifts $\Delta \delta_{max}$ and the association constants K_a (Table 1) were determined by the use of ¹H NMR titration experiments as described in the Section 4.

Table 1. Comparison of $\Delta \delta_{max}$ and K_a (M⁻¹) for the formation of the complexes between TNF-C₆₀:ECZ and TNDCF-C₆₀:ECZ in CDCl₃ at 25 °C

	$\Delta \delta_{ m max}$	$K_{\rm a} ({ m M}^{-1})$	
TNF-C ₆₀	$\begin{array}{c} 0.59 \ (\mathrm{H}^{1}) \\ 1.14 \ (\mathrm{H}^{3}) \\ 0.98 \ (\mathrm{H}^{6}) \\ 1.25 \ (\mathrm{H}^{8}) \end{array}$	5.1±0.9	
TNDCF-C ₆₀	$\begin{array}{c} 1.36 \ (\mathrm{H}^{\mathrm{o}}) \\ 1.36 \ (\mathrm{H}^{1}) \\ 0.50 \ (\mathrm{H}^{3}) \\ 0.93 \ (\mathrm{H}^{6}) \\ 1.73 \ (\mathrm{H}^{8}) \end{array}$	21.3±0.6	

Job plot analyses were performed to determine the stoichiometry of the complexes **2**:ECZ and **3**:ECZ. In the case of the **3**:ECZ complex, the plot of the mole fraction χ ($\chi = [ECZ]_0/[3]_0 + [ECZ]_0$) versus the mole fraction multiplied by the complexation-induced ¹H NMR shift of ECZ, $\chi \Delta \delta_{obs}$, shows a maximum at $\chi = 0.5$, which equates to a 1:1 stoichiometry for the complex (Fig. 5).



Figure 5. The job plot of the complex TNDCF–C₆₀:ECZ (proton H⁸ of **3** is reported. The fitting line is calculated with the parameters: $\Delta \delta_{\text{max}} = 1.73$ and $K_{\text{a}} = 21.3 \pm 0.6 \text{ M}^{-1}$.

2.3. Square wave voltammetric studies

Electrochemical Osteryoung square wave voltammetric (OSWV) studies of compounds 2 and 3, and their respective reference compounds 10 and 11, showed reduction waves corresponding to both the TNF and *N*-methylfulleropyrrolidine moieties (see Table 2, Figs. 6 and 7). In both cases, the first reduction was slightly shifted anodically, suggesting only a very small interaction between the

Table 2. Electrochemical reduction data for fluorene derivatives

	Reduction (V) versus Fc					
	E1/2(I)	<i>E</i> 1/2(II)	E1/2(III)	<i>E</i> 1/2(IV)	<i>E</i> 1/2(V)	
2	-0.80	-1.01	-1.13	-1.56	-1.94	
10 3	-0.82 - 0.45	-1.17 -1.02	-2 -1.56	-1.78		
11	-0.46	-1.03	-1.81			



Figure 6. OSWV of (a) compound 10 and (b) compound 2 (impurity designated by *).



Figure 7. OSWV of (a) compound 11 and (b) compound 3 (impurities designated by *).

fullerene and the substituent. For compound **3**, the second TNF-based reduction overlapped with the first fullerene-based reduction, resulting in a 2-electron wave.

The sequential addition of *N*-ethylcarbazole, up to a 100-fold excess, to the solution of compound 2 (Fig. 8) caused a cathodic shift in the first TNF-based reduction of



Figure 8. OSWV of compound 2 before (thin line) and after (thick line) addition of 100 equiv of *N*-ethylcarbazole.

38 mV, thus confirming the NMR results suggesting that the π -donor formed a complex with 2, which increased the electron density on the TNF moiety. The first fullerenebased reduction was also shifted by a comparable amount, which is reasonable since C_{60} is also known to be a good electron acceptor. As a result, the already reduced fluorenone moiety would exhibit a strongly decreased ability to interact with ECZ. In the case of compound 3, after addition of 100 equiv of N-ethylcarbazole (Fig. 9), the first TNF-based reduction was shifted cathodically by 70 mV, while the fullerene-based first reduction did not shift. This observation can be rationalized on the basis of the increased electron-accepting ability due to the two cyano groups on the TNF moiety, which increases dramatically its electron-accepting ability as compared to that of compound 2 to such an extent, that the reduced fluorene moiety still interacts stronger with ECZ than the fullerene one does.



Figure 9. OSWV of compound 3 before (thin line) and after (thick line) addition of 100 equiv of *N*-ethylcarbazole.

Preliminary results of the photorefractive performance of these compounds as sensitizers in polymer composites based on poly(*N*-vinylcarbazole) are similar to that of C_{60} , but with shorter response times and slightly lower gain coefficients. A more detailed study of these experiments is out of the scope of this article and will be published elsewhere.

3. Conclusion

We have prepared and characterized the new C₆₀-fluorene adducts **2** and **3** bearing a flexible chain. UV-vis and electrochemical studies indicate the absence of interaction between both moieties in the ground state. However, addition of an excess of the π -donor ECZ to solutions of compounds **2** and **3** affords complexes in which the carbazole interacts with the fluorene moiety, as detected by NMR and OSWV.

4. Experimental

4.1. General

The chemical reagents were purchased reagent-grade from Aldrich Corporation and were used without further purification unless otherwise stated. All solvents were purified using standard procedures. Column Chromatography: SiO₂ (40–63 μ m). TLC plates coated with SiO₂ 60F254 were visualized by UV light. UV–vis spectra were recorded with a Helios Gamma spectrophotometer and IR spectra with a Nicolet Impact 400D spectrophotometer. NMR spectra were measured with a Bruker AC 300 and with a Bruker AVANCE DRX-500. Mass spectra were obtained from a Bruker Reflex III matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometer. Elemental analysis were performed on a Thermo Finnigan Flash 1112 CHN elemental analyzator.

The electrochemical measurements of compounds 2 and 3 including the model compounds methyl 2,5,7-trinitrofluorenone-4-carboxylate (10, MTNFC) and methyl 2,5, 7-trinitrodicyanomethylenfluorene-4-carboxylate (11, MTNDCM), were performed in a one-compartment electrochemical cell in oxygen-free tetrahydrofuran (THF) using a CHI 660A electrochemical workstation. For all experiments, a 0.7 mM sample concentration was analyzed. A platinum disk (1 mm) was used as the working electrode and a platinum wire as the counter electrode. A silver wire immersed in the solvent mixture with 0.1 M supporting electrolyte and 0.01 M AgNO₃ separated from the bulk of the solution by a Vycor glass served as the pseudo-reference electrode. The supporting electrolyte used was tetrabutylammonium hexafluorophosphate, TBAPF₆ (0.1 M, Fluka, >99%). Ferrocene was added as an internal standard, and all redox waves are referenced to the Fc/Fc^+ redox couple.

4.1.1. Synthesis of 11-hydroxy-3,6,9-trioxaundecyl *p*-formylbenzoate (4). A mixture of 4-formylbenzoic acid (1.97 g, 13.1 mmol), tetraethylene glycol (13.47 g, 69.4 mmol), *N*,*N*-dicyclohexylcarbodiimide (2.79 g, 4-(dimethylamino)pyridine 13.5 mmol), (160 mg, 1.3 mmol) and dry toluene (50 ml) was stirred at 65 °C under argon atmosphere for 5 h. The reaction mixture was cooled and a white solid was filtered off. The organic solution obtained was washed several times with water, dried, concentrated under vacuum, and the crude material was purified by column chromatography (eluent CH₂Cl₂/ CH₃OH 15:1) to afford the product as a colourless oil (2.54 g, 59%). FT-IR (Ge-ATR) ν_{max} 3457, 1738, 1367, 1216, 1102 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 10.09 (s, 1H, CHO), 8.21 (d, 2H, J = 8.6 Hz, H-Ar), 7.94 (d, 2H, J = 8.6 Hz, H-Ar), 4.51 (t, 2H, J = 4.8 Hz, O=C-OCH₂), 3.84 (t, 2H, J=4.8 Hz, O=C-OCH₂-CH₂), 3.58-3.71 (m, 13H, OH, $6 \times O$ -CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 191.5, 165.3, 138.9, 134.8, 130.0, 129.2, 72.3, 70.4, 70.3, 70.0, 68.8, 64.4, 61.4. FAB-MS: m/z: 327 ([M+1]⁺). Anal. Calcd for C₁₆H₂₂O₇: C, 58.89; H, 6.80. Found: C, 58.14; H, 7.04.

4.1.2. Synthesis of $11-(2',5',7'-\text{trinitrofluorenone-4'-carboxylate)-3,6,9-trioxaundecyl$ *p*-formylbenzoate (6). A mixture of**4**(790 mg, 2.1 mmol), 2,5,7-trinitro-fluorenone-4-carboxylic acid chloride (690 mg, 2.1 mmol), DMAP (20 mg, 0.2 mmol) and dichloromethane (25 ml) was stirred for 48 h under argon at room temperature. The reaction mixture was washed with sodium bicarbonate solution and water. After the solvent was evaporated under reduced pressure, the crude material was purified by column

chromatography (eluent hexane/ethyl acetate 1:2), to yield the pure product as an orange oil (500 mg, 35%). FT-IR (Ge-ATR) ν_{max} 1724, 1540, 1347 1277, 1103 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 10.07 (s, 1H, CHO), 8.94 (d, 1H, J=2.1 Hz, H-TNF), 8.89 (d, 1H, J=2.2 Hz, H-TNF), 8.81 (d, 1H, J=2.1 Hz, H-TNF), 8.75 (d, 1H, J=2.2 Hz, H-TNF), 8.18 (d, 2H, J=8.3 Hz, H-Ar), 7.92 (d, 2H, J= 8.3 Hz, H-Ar), 4.53–4.47 (m, 4H, 2×CH₂–O–C=O), 3.88-3.83 (m, 4H, 2×CH₂-CH₂-O-C=O), 3.73-3.67 (m, 8H, $4 \times CH_2$ –O). ¹³C NMR (125 MHz, CDCl₃) δ 191.3, 184.6, 165.0, 164.1, 149.2, 149.0, 146.2, 143.1, 139.3, 138.8, 138.5, 137.4, 134.6, 131.7, 130.4, 129.9, 129.1, 125.0, 122.1, 121.4, 70.3, 68.7, 68.2, 65.8, 64.3. MALDI-TOF (dithranol+NaI): m/z: 690 ([M+Na]⁺). Anal. Calcd for $C_{30}H_{25}N_3O_{15}$: C, 53.98; H, 3.78; N, 6.29. Found: C, 53.9; H, 4.13; N, 5.72.

4.1.3. Synthesis of 11-(2',5',7'-trinitrofluorenone-4'carboxylate)-3,6,9-trioxaundecyl p-(N-methyl-3,4-fulleropyrrolidin-2-yl)benzoate (2). A mixture of C₆₀ (180 mg, 0.3 mmol), 6 (500 mg, 0.7 mmol), sarcosine (70 mg, 0.8 mmol) and 1,2-dichlorobenzene (30 ml) was heated under argon for 7 h. After flash chromatography (eluent toluene/diethyl ether 9:1) the desired product was isolated as a brown solid (110 mg, 31%). ¹H NMR (300 MHz, CDCl₃) δ 8.95 (d, 1H, J=2.1 Hz, H–TNF), 8.90 (d, 1H, J=2.2 Hz, H–TNF), 8.82 (d, 1H, J=2.1 Hz, H–TNF), 8.75 (d, 1H, J= 2.2 Hz, H-TNF), 8.10 (d, 2H, J=8.1 Hz, H-Ar), 7.90 (m, 2H, H-Ar), 5.01 (d, 2H, J=9.6 Hz, CHHN), 5.00 (s, 1H, CHN), 4.53 (t, 2H, J=4.7 Hz, TNF-CO₂-CH₂), 4.43 (t, 2H, J = 4.9 Hz, Ar-CO₂-CH₂), 4.29 (d, 1H, J = 9.6 Hz, CHHN) 3.91-3.63 (m, 12H, 6×CH₂-O), 2.81 (s, 3H, N-CH₃). ¹³C NMR (125 MHz, CDCl₃) δ 184.6, 166.2, 164.3, 155.9, 153.7, 152.8, 152.6, 149.4, 149.1, 147.3, 147.2, 146.4, 146.3, 146.2, 146.1, 146.0, 145.9, 145.7, 145.6, 145.4, 145.3, 145.2, 145.1, 144.6, 144.5, 144.3, 143.2, 143.1, 142.9, 142.6, 142.5, 142.4, 142.1, 142.0, 141.9, 141.8, 141.7, 141.6, 141.5, 140.1, 139.8, 139.4, 139.3, 138.5, 137.4, 136.9, 136.3, 135.9, 135.6, 131.8, 130.5, 130.0, 129.0, 125.0, 122.2, 21.6, 83.0, 70.6, 70.0, 69.0, 68.5, 66.1, 65.8, 64.1, 40.0. FT-IR (KBr) v_{max} 1736, 1613, 1594, 1538, 1343, 1093 cm⁻¹. MALDI-TOF (dithranol): m/z: 1415 ([M+1]⁺), 695 ([M+1]⁺-C₆₀). Anal. Calcd for C₉₂H₃₀N₄O₁₄: C, 78.08; H, 2.14; N, 3.96. Found: C, 78.12; H, 2.55; N, 3.90.

4.1.4. Synthesis of 11-(2',5',7'-trinitro-9'-dicyanomethylenfluorene-4'-carboxylate)-3,6,9-trioxaundecyl p-(N-methyl-3,4-fulleropyrrolidin-2-yl)benzoate (3). A mixture of 2 (30 mg, 0.02 mmol), malononitrile (20 mg, 0.3 mmol) and dry DMF (20 ml), was stirred under argon at room temperature for 72 h. The reaction mixture was diluted with ethyl acetate and washed with brine and water. The organic layer was dried, concentrated and the residue was washed with methanol and diethyl ether to give the product as a brown solid (20 mg, 64%). FT-IR (KBr) $\nu_{\rm max}$ 2199, 1720, 1611, 1537, 1342, 1104 cm⁻¹. ¹H NMR (300 MHz, CDCl₃,) δ 9.69 (d, 1H, J=1.8 Hz, H–TNDCF), 9.60 (d, 1H, J = 2.0 Hz, H-TNDCF, 8.98 (d, 1H, J = 1.9 Hz,H-TNDCF), 8.93 (d, 1H, J=2.1 Hz, H-TNDCF), 8.06 (d, 2H, J=8.9 Hz, H-Ar), 7.91 (m, 2H, H-Ar), 4.99 (d, 2H, J=9.6 Hz, CHHN), 4.99 (s, 1H, CHN), 4.48 (t, 2H, J=4.8 Hz, TNDCF-CO₂-CH₂, Ar-CO₂-CH₂), 4.35 (t, 2H, J =5.1 Hz, 4.28 (d, 1H, J = 9.6 Hz, CHHN) 3.84-3.62 (m, 12H, 12H)

6×CH₂–O), 2.81 (s, 3H, N–CH₃). ¹³C NMR (125 MHz, CDCl₃) δ 166.3, 164.1, 156.0, 153.8, 153.3, 152.9, 152.7, 149.2, 148.7, 147.3, 146.9, 146.5, 146.3, 146.2, 146.1, 145.9, 145.8, 145.7, 145.5, 145.4, 145.3, 145.2, 145.1, 144.7, 144.5, 144.4, 144.3, 143.1, 143.0, 142.6, 142.5, 142.2, 142.1, 142.0, 141.9, 137.6, 137.0, 136.4, 136.0, 135.9, 135.6, 132.5, 130.3, 130.0, 129.0, 124.6, 123.7, 123.0, 111.5, 111.4, 83.1, 70.7, 70.0, 69.2, 69.1, 68.6, 66.3, 65.8, 64.1, 40.0. MALDI-TOF (dithranol): m/z: 1463 ([M+1]⁺), 743 ([M+1]⁺ – C₆₀). Anal. Calcd for C₉₅H₃₀N₆O₁₃: C, 77.98; H, 2.07; N, 5.74. Found: C, 77.47; H, 2.36; N, 5.81.

4.1.5. Synthesis of methyl 2,5,7-trinitrofluorenone-4carboxylate (10). To a mixture of 2,5,7-trinitrofluorenone-4-carboxylic acid (400 mg, 1.1 mmol), DCC (280 mg, 1.4 mmol), DMAP (10 mg, 0.1 mmol) in 10 ml of dry toluene, 0.45 ml (11.1 mmol) of dry methanol were slowly added. The mixture was heated at 65 °C for 20 h under argon atmosphere. After the solvent was evaporated, the crude material was purified by column chromatography (eluent hexane/ethyl acetate 4:1), to afford the pure product as a pale yellow solid (210 mg, 51%). FT-IR (KBr) ν_{max} 1736, 1616, 1594, 1543, 1345 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 8.97 (d, 1H, J=2.1 Hz, H–TNF), 8.89 (d, 1H, J=2.2 Hz, H–TNF), 8.83 (d, 1H, J=2.1 Hz, H–TNF), 8.78 (d, 1H, J=2.2 Hz, H–TNF), 4.00 (s, 3H, CO₂CH₃).

4.1.6. Synthesis of methyl 2,5,7-trinitro-9-dicyanomethylenfluorene-4-carboxylate (11). A mixture of 10 (100 mg, 0.3 mmol), malononitrile (100 mg, 1.5 mmol) and dry DMF (5 ml), was stirred and heated at 50 °C, under argon, for 14 h. The reaction mixture was diluted with ethyl acetate and the residue was washed with brine and water. The organic layer was dried, concentrated and washed with methanol to give the product as a yellow-green solid (70 mg, 62%). FT-IR (KBr) ν_{max} 2232, 1734, 1602, 1536, 1350 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.70 (d, 1H, J= 1.9 Hz, H–TNDCF), 9.62 (d, 1H, J=2.0 Hz, H–TNDCF), 9.00 (d, 1H, J=1.8 Hz, H–TNDCF), 8.91 (d, 1H, J= 2.0 Hz, H–TNDCF), 4.00 (s, 3H, CO₂CH₃).

Determination of K_a : ¹H NMR titration method

The uncomplexed dyad (Host, H) and ethylcarbazole (Guest, G) are in equilibrium with the 1:1 complex (C)

$$H + G \rightleftharpoons C$$

The association constant K_a is defined by Eq. 1

$$K_{a} = \frac{[C]}{[H][G]} \tag{1}$$

and can be rewritten as Eq. 2

$$K_a = \frac{[C]}{([H_0] - [C])([G_0] - [C])}$$
(2)

where $[H_0]$ and $[G_0]$ are the starting concentrations of the dyad and *N*-ethylcarbazole, respectively.

Under fast-exchange conditions the observed chemical shift δ_{obs} of the dyad will be an averaged value between free (δ_{H})

and complexed host ($\delta_{\rm C}$), as we can see in Eq. 3

$$\delta_{\rm obs} = \frac{[{\rm H}]}{[{\rm H}] + [{\rm C}]} \delta_{\rm H} + \frac{[{\rm C}]}{[{\rm H}] + [{\rm C}]} \delta_{\rm C}$$
(3)

Combination of Eqs. 2 and 3 leads to Eq. 4, that gives the observed shift for the host as a function of [H₀], [G₀], $\delta_{\rm H}$, $\delta_{\rm C}$ and $K_{\rm a}$

$$\delta_{\text{obs}} = \delta_{\text{H}} - \frac{\delta_{\text{H}} - \delta_{\text{C}}}{2} \left[\left(1 + \frac{[G_0]}{[H_0]} + \frac{1}{[H_0]K_a} \right) - \sqrt{\left(1 + \frac{[G_0]}{[H_0]} + \frac{1}{[H_0]K_a} \right)^2 - 4\frac{[G_0]}{[H_0]}} \right]$$
(4)

The NMR studies were performed on a Bruker Avance DRX 500 MHz at 298 ± 1 K in CDCl₃, the concentration of the dyad was fixed at 0.99×10^{-3} and 0.83×10^{-3} M for dyad **2** and dyad **3**, respectively. Increasing amounts of ECZ were added while the total volume of the resulting solution was kept constant (0.5 ml), and the complexation-induced shift of the protons of the fluorene moiety (δ_{obs}) were observed. Fitting of these data to the 1:1 binding isotherm by iterative methods²⁵ delivered the parameters K_a and $\Delta \delta_{max} = \delta_H - \delta_C$.

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- 25. A nonlinear regression analysis of Eq. 4 (see Section 4) was performed by the program OriginPro 7.5.