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Nanosized Rigid π-Conjugated Molecular Heterojunctions with Multi[60]fullerenes: Facile Synthesis and Photophysical Properties

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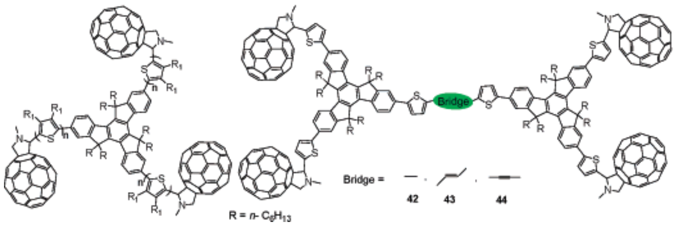

A series of large, rigid, new, well-defined, D−π-B−A compounds with three chromophores (truxene moieties at the core, conjugated oligothiophenes as the branch bridges, and [60]pyrrolidinofullerene (C_{60}) segments as the end-capped groups) have been facilely developed in this contribution. Oligothiophene-functionalized truxene derivatives **1**−**29** are prepared by the Suzuki, the Sonogashira, and the Negishi cross-coupling reactions catalyzed by $Pd(PPh_3)_4$ as well as the McMurry reaction, respectively. The 1,3-dipolar cycloaddition of the oligomers with C_{60} and *N*-methylglycine yields a new family of star-shaped D−π−B−A derivatives end-capped with pyrrolidinofullerene moieties as the active materials for photovoltaic devices in which one, two, three, or four C_{60} moieties are allocated at the peripheral position of well-defined compounds, respectively. We also investigate the UV−vis and photoluminescence behaviors of these pyrrolidinofullerene-functionalized derivatives. The emission is obviously quenched after the inducement of the C_{60} moieties. We also observe that the emission intensity is decreased with the increase in the number of C_{60} moieties.

Introduction

Particularly, extended π-conjugated star-shaped molecules with definite nanometer sizes and intrinsic stiff nature have been proved to exhibit interesting electrical, optical, nonlinear optical, and electroluminescent properties for applications in electronic and photoelectronic devices, including organic photovoltaic devices[1] and organic light-emitting diodes.[2] One of the important challenging goals of star-shaped and dendritic materials chemistry is to develop new families of π-conjugated star-shaped molecules with novel branches and cores, to investigate their physical and chemical properties, as well as to understand the structure−property relationship within such structures. In comparison to their corresponding linear analogues, star-shaped molecules have a number of advantages for applications in photoelectronic devices, for example, the well-defined, unique macromolecular structure, good film-forming processing, and other fascinating properties.[3]

Composite films consisting of organic π-conjugated materials and fullerenes (C_{60}) derivatives have currently been extensively

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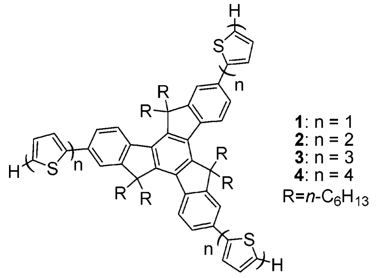
investigated in photovoltaic cells with the aim of generating larger-area photodetector and solar cells.[4,5] In the past several years, integration of some chromophores, including well-defined linear[4] or star-shaped compounds,[1a,b] and fixing fullerenes as terminal groups in conjugated oligomeric systems through covalent bonds have gained considerable attention to lead to high conversion efficiencies for plastic solar cells.[1] However, it is still imperative to develop novel fullerene-functionalized π-conjugated star-shaped molecules and to understand the effect of the content of pyrrolidinofullerene covalent bonding at the bridge on the properties of desired materials and the relationship between the properties and the intrinsic structure of materials. Most recently, the spherical wheels based on fullerene-C_{60} and freely rotating axles based on alkynes were utilized for directed single-molecular nanoscale rolling.[6]

The heptacyclic polyarene 10,15-dihydro-*5H*-di-indeno[1,2-*a*;1′,2′-*c*]fluorene (truxene, Tr), as one of the family of polycyclic aromatic hydrocarbons, has been recognized as a potential starting material for the construction of large polyarenes and bowl-shaped fragments of the fullerenes and of C_3 tripods materials in asymmetric catalysis, chiral recognition, and liquid crystal as well as photonic and electronic displays due to a polyarene and planar system.[7] In our group, we have also developed a novel series of π-conjugated star-shaped and dendritic materials based on truxene from the viewpoint of fundamental chemistry as well as practical applicants in organic optics and electronics.[8]

SCHEME 1



Herein, we describe a facile strategy to precisely employ various coupling reactions for preparing a novel type of D−π−B−A, well-defined, star-shaped, conjugated oligomers with three chromophores (the truxene moiety, rigid oligothiophenes as the branch bridges and fullerene as the end-capped groups). The conjugation length of the oligothiophenes in bridges and the content of capped fullerene groups have been systematically moderated. The molecular design allows for probing effects of various contents of fullerenes on the properties of materials and on intramolecular and intermolecular energy transfer. The divergent constitution facilitates the construction of well-defined energy gradients via a site-specific functionalization and an array of light-collecting chromophores at one periphery toward one or multienergies or electron sinks in another periphery. Through the investigations of electric and optical properties, we can understand how the significant photoinduced intramolecular electronic communication or intermolecular charge transfer between the hosts and *N*-methylpyrrolidinofullerene moieties have formed in the excited states or in the ground states.

Results and Discussion

Synthesis. The Synthesis of Star-Shaped Aldehydes. First, we developed a series of novel star-shaped molecules. Scheme 1 outlines the star-shaped structures of **1**−**4**, prepared through the Suzuki reaction in our previous contribution.[8a] To further improve the solubility of our desired fullerene-functionalized triads in common organic solvents, we utilized the 3,4-ethylenedioxythiophene (EDOT) moiety instead of the thiophene moiety. Scheme 2 illustrates the synthetic route to compounds **5** and **6**. In place of the Suzuki cross-coupling reaction, we

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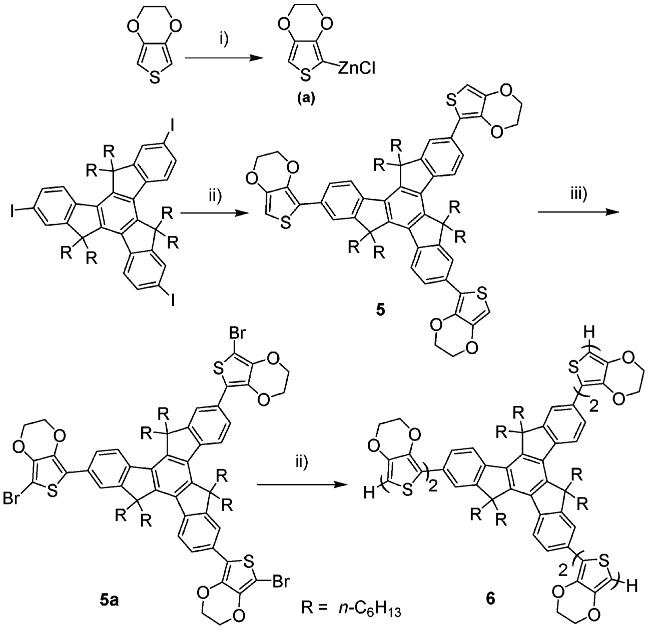
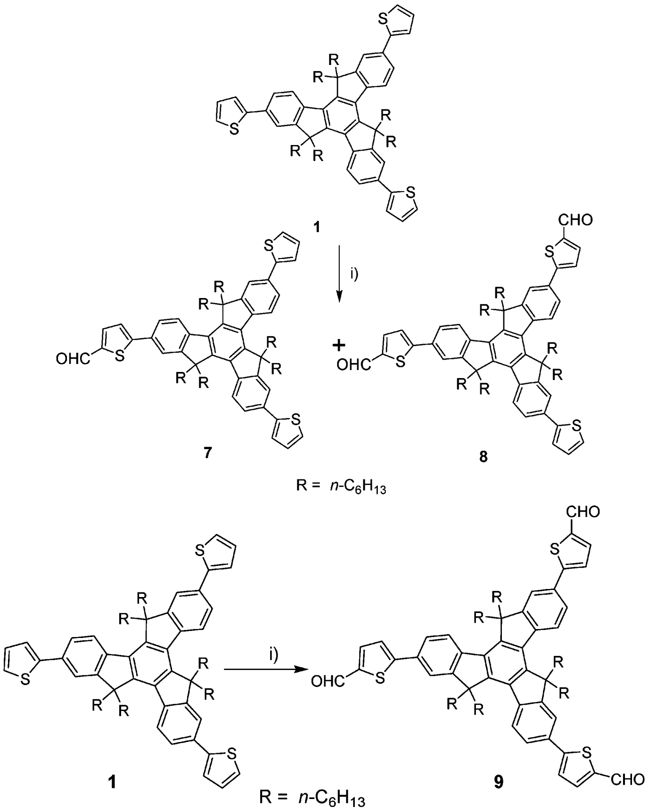
SCHEME 2 [a]



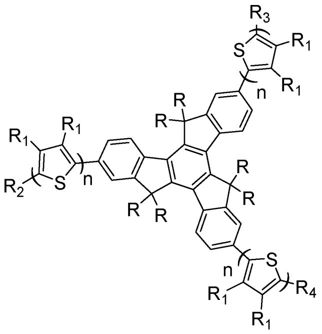
[a] Reagents and condition: (i) LDA, THF, −78 °C; $ZnCl_2$, THF, −78 °C to rt; (ii) $Pd(PPh_3)_4$, THF, reflux, 10 h, 86% for **5**, 24% for **6**; (iii) NBS, $CHCl_3/CH_3COOH$ (1/1), 0 °C, 76%.

SCHEME 3 [a]



[a] Reagents and conditions for **1** to **7** and **8**: (i) DMF (1.1 equiv), $POCl_3$ (1.0 equiv), DCE, reflux, 3 h, 46% for **7**, 20% for **8**. Reagents and conditions for **1** to **9**: (i) DMF (15 equiv), $POCl_3$ (12 equiv), DCE, reflux, 10 h, 85%.

SCHEME 4



Cmps.	R_1	R_2	R_3	R_4	n
7	H	CHO	H	H	1
8	H	CHO	CHO	H	1
9	H	CHO	CHO	CHO	1
10	H	CHO	H	H	2
11	H	CHO	CHO	H	2
12	H	CHO	CHO	CHO	2
13	H	CHO	CHO	CHO	3
14	H	CHO	CHO	CHO	4
15	OCH_2	CHO	H	H	1
16	OCH_2	CHO	CHO	H	1
17	OCH_2	CHO	CHO	CHO	1
18	OCH_2	CHO	CHO	CHO	2

employed the Negishi cross-coupling reaction between 5,5′,-10,10′,15,15′-hexahexyl-2,7,12-triiodo-10,15-dihydro-*5H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene[8a] and EDOT-2-zinc chloride (**a**) catalyzed by $Pd(PPh_3)_4$ to afford **5** in about 86% yield. EDOT-2-zinc chloride (**a**) was in situ derived from the lithiation of EDOT with LDA, followed by reacting with anhydrous $ZnCl_2$ in anhydrous THF. After following regioselective bromination of the α-positions at the thiophene moieties by NBS, we also prepared **6** bearing 5,2′-bis(EDOT) arms at three branches through the similar Negishi cross-coupling procedures in 24% yields.

By the Vilsmeier reaction, we not only got trialdehyde derivatives by adding an excess of phosphorus oxychloride ($POCl_3$) in high yields, but also could obtain the monoaldehydes and dialdehydes by controlling the added amount of $POCl_3$, respectively. As outlined in Scheme 3, oligothiophene-functionalized star-shaped truxene derivative **1** was subjected to the Vilsmeier reaction at one of the focal points with DMF and $POCl_3$ in refluxed 1,2-dichloroethane to give the corresponding aldehydes **7**−**9** in good yields. We also obtained other star-shaped aldehydes **10**−**18** by employing the same procedures. The structures of all new star-shaped aldehydes **7**−**18** are shown in Scheme 4.

As shown in Scheme 5, the Suzuki coupling reaction between the readily available 5,5′,10,10′,15,15′-hexahexyl-2,7,12-tribromo-10,15-dihydro-*5H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene[8a] and 2-thiopheneboronic acid, with $Pd(PPh_3)_4$ as the catalyst in THF, afforded both **19** and **20** in moderate yield, which were easily separated by column chromatography. The homocoupling of **19** with LDA/$CuCl_2$ provided dimer **21** in 65% yield.[9] The following Suzuki coupling reaction between **21** and 2-thiopheneboronic acid catalyzed by $Pd(PPh_3)_4$ afforded **22** in 90% yield.

As illustrated in Scheme 6, the McMurry reaction of **7** utilizing $TiCl_4$−Zn produced **23** with a double-bond linker in 72% yield.[10] As shown in Scheme 7, the same formylation of **22** and **23** using DMF and $POCl_3$ conveniently afforded the corresponding tetraaldehydes, **24** and **25**, the other two precursors of the C_{60} dyads, respectively.

Scheme 8 outlines the synthetic approach to compound **27**. The Suzuki reaction between **20** and 5-(trimethylsilyl)-2-thienylboronic acid[11] afforded **26** in good yield. Compound **26** reacted with ICl in a mixture of methylene chloride and diethyl ether at 0 °C to give the monoiodide compound followed by the Sonogashira coupling with acetylene gas, which afforded the desired dimer **27** linking with the ethynylene group in 50%

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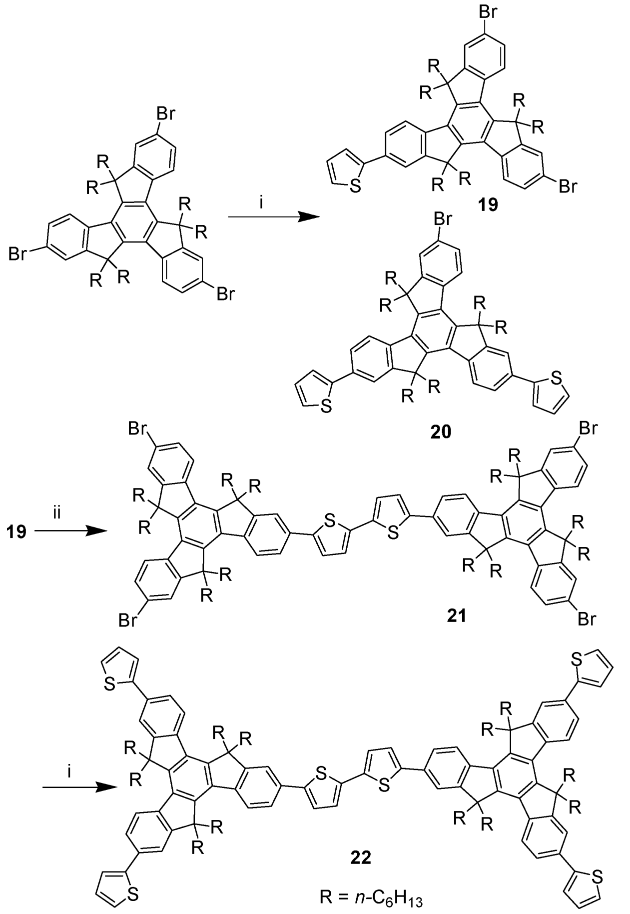
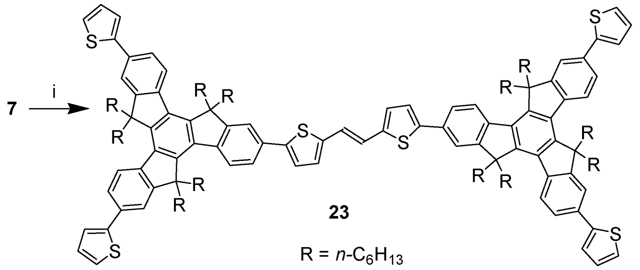
SCHEME 5 [a]



[a] Reagents and conditions: (i) 2-thiopheneboronic acid, Na_2CO_3 (2 M), $Pd(PPh_3)_4$, THF, reflux, 36% for **19**, 24% for **20**, 90% for **22**; (ii) (a) LDA, −78 °C, 1 h; (b) $CuCl_2$, −78 °C to rt, 10 h, 65%.

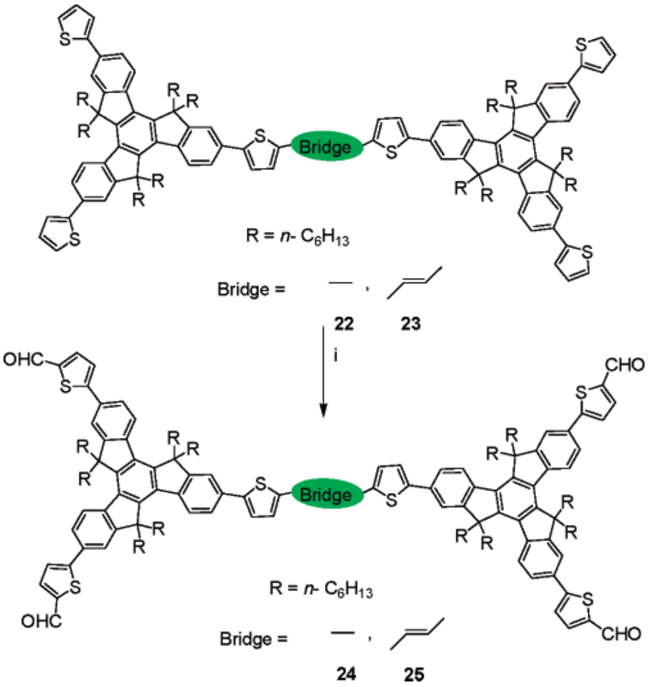
SCHEME 6 [a]



[a] Reagents and conditions: (i) $TiCl_4$−Zn, THF, reflux, 16 h, 72%.

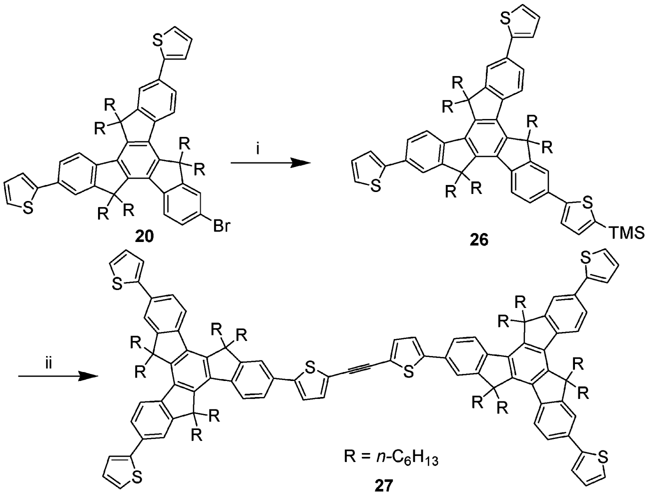
yield.[12] As shown in Scheme 9, the treatment of **8** with *N*-iodosuccinimide afforded **28**.[13] The same Sonogashira coupling between **28** and acetylene gas conveniently afforded another tetraaldehyde **29**.

SCHEME 7 [a]



[a] Reagents and conditions: (i) DMF (30 equiv), $POCl_3$ (25 equiv), DCE, reflux, 12 h, 83% for **24** and **25**.

SCHEME 8 [a]



[a] Reagents and conditions: (i) 2-trimethylsilyl)-5-thienyl boronic acids, $Pd(PPh_3)_4$, 70 °C, Na_2CO_3 (2 M), THF, 10 h, 90%; (ii) (a) ICl, CH_2Cl_2, ether, 0 °C, 1 h; (b) acetylene, CuI, Et_3N, $PdCl_2(PPh_3)_2$, rt, 8 h, 50%.

Synthesis of C$_{60}$-Functionalized Dyads. As outlined in Schemes 10−12, we prepared the star-shaped donor−acceptor C$_{60}$-functionalized dyads **30**−**44** by treating the aldehydes with fullerene and an excess of *N*-methylglycine in refluxing chlorobenzene through 1,3-dipolar cycloaddition reactions.[14] The yields were about 45−55% for the monoadducts, 40−47% for the bisadducts, and about 20% for the triadducts and tetraadducts. Because of the presence of the long alkyl chains, most of the C$_{60}$ adducts were readily soluble in polar organic solvents. In addition, those bearing EDOT moieties exhibited good solubility in common organic solvents at room temperature.

Not only did we obtain appropriate ^{1}H and ^{13}C NMR spectra as well as elemental analytical data, we also employed MALDI-

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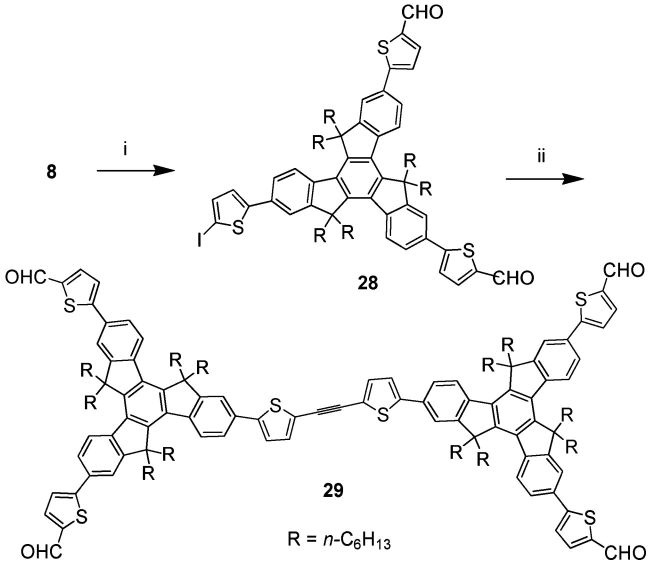
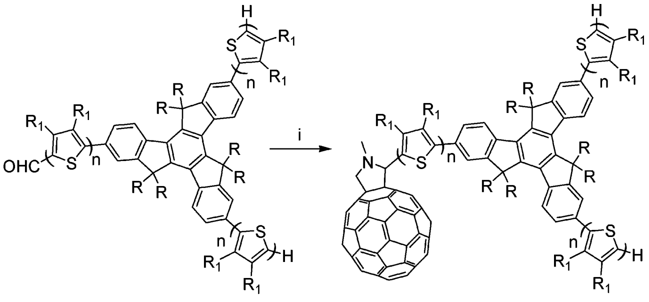
SCHEME 9 [a]



[a] Reagents and conditions: (i) NIS, CH_2Cl_2/AcOH, 0 °C, 2 h, 90%; (ii) acetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 8 h, rt, 45%.

SCHEME 10 [a]



Cmps.	R_1	n
7	H	1
10	H	2
15	OCH_2	1

Cmps.	R_1	n	Yield
30	H	1	55%
31	H	2	50%
32	OCH_2	1	51%

[a] Reagents and conditions: (i) N-methylglycine, C_{60}, chlorobenzene, reflux, 12 h.

TOF MS measurements to characterize the structure and molecular weight for every new compound. About C_{60} adducts, all adducts containing more than one fullerene unit have been obtained as mixtures of diasteroisomers, which can be separated in some cases. However, we obtained all C_{60} adducts as mixtures of diastereomers as a result of the creation of a stereocenter at each pyrrolidine ring. From ^{1}H NMR spectra, we did not observe any self-association by arene stacking in solutions[15] with an increase in the concentration. This indicated that hexahexyl substituents efficiently reduced such self-association in solutions, which was also in agreement with the results investigated by the optical properties. Our described results also provided a versatile strategy for controlling the morphology of the truxene derivatives.

Thermal Stability. For photoelectronic applications, the thermal stability of organic materials is critical for device stability and lifetime. The degradation of organic photoelectronic devices depends on morphological changes resulting from the thermal instability of the amorphous organic layer.[16] The morphological change might be promoted by the rapid molecular motion near the glass transition temperature (T_g). In our investigation, all compounds including C_{60} adducts exhibited an onset of evaporation or decomposition greater than 300 °C with no weight loss at lower temperature. All compounds were in an amorphous state at room temperature. The glass transition temperatures were improved from 40 °C for **1** to 170 °C for **6**. We observed that the glass transition augmented from **1** to **4** with the increase of the conjugation length. Moreover, the T_g of EDOT derivatives was higher than that of the corresponding nonsubstituted thiophene derivatives. However, all C_{60} adducts did not exhibit any obvious glass transition during the heating. We observed that **1**−**6** formed kinetically stable amorphous phases after thermal annealing. Typically, differential scanning calorimetric thermogram characteristics of **1**−**6** are shown in Figure 1 for elucidation.

Photophysical Properties. Normally, oligothiophenes and polythiophenes show a strong $\pi-\pi^*$ electron absorption band in the visible region, which is progressively red-shifted with increasing chain length. On the basis of the spectroscopic investigation of oligothiophenes, the effective conjugation length is not much longer than 11 repeat units.[17] We first investigated the basic optical properties of **1**−**6** in dilute THF solutions. The absorption and emission spectra of **1**−**6** in THF solutions are shown in Figure 2. As summarized in Table 1, the continuous red shifts of the absorption spectra were observed with a successive increase of the thiophene ring in the investigation of the oligothiophene-functionalized truxene derivatives. Compounds **1**−**4** exhibited the maximum absorption peaks at 341, 383, 411, and 424 nm and were substantially red-shifted relatives to thiophene, bithiophene (302 nm), terthiophene, (354 nm) and quaterthiophene (396 nm), respectively.[8a] The electronic absorption maximum for **4** (424 nm) was quite close to that of the regioregular polyalkylthiophenes (434 nm).[8a] The results suggested the formation of a highly extended π-delocalized system through the truxene core. For **5**, the absorption behaviors peaked at 347 nm, with a shoulder at 363 nm that red-shifted at about 6 nm in comparison with that of compound **1**. This was due to the electron-donating effect of the ethylenedioxy substituents at the thiophene rings. Similarly, compared with the corresponding **2**, the absorption spectrum of **6** also red-shifted and exhibited the maximum peaks at 398 and 420 nm, which were close to that of **3**. For these two series of compounds, the absorption spectra of **5** and **6** showed the more well-defined vibronic behavior in comparison with those of **1**−**4**.

For PL spectra of all compounds, we observed that they showed a maximum with a well-defined vibronic feature and that the difference of peaks became more conspicuous with the increase in the thiophene rings. The emission spectra for **1**−**6** in THF solution are shown in Figure 3. The PL behaviors of these compounds showed similar features as those of the absorption spectra. The maximum peak red-shifted with the increase in the effective conjugated length from **1** to **4**. Although

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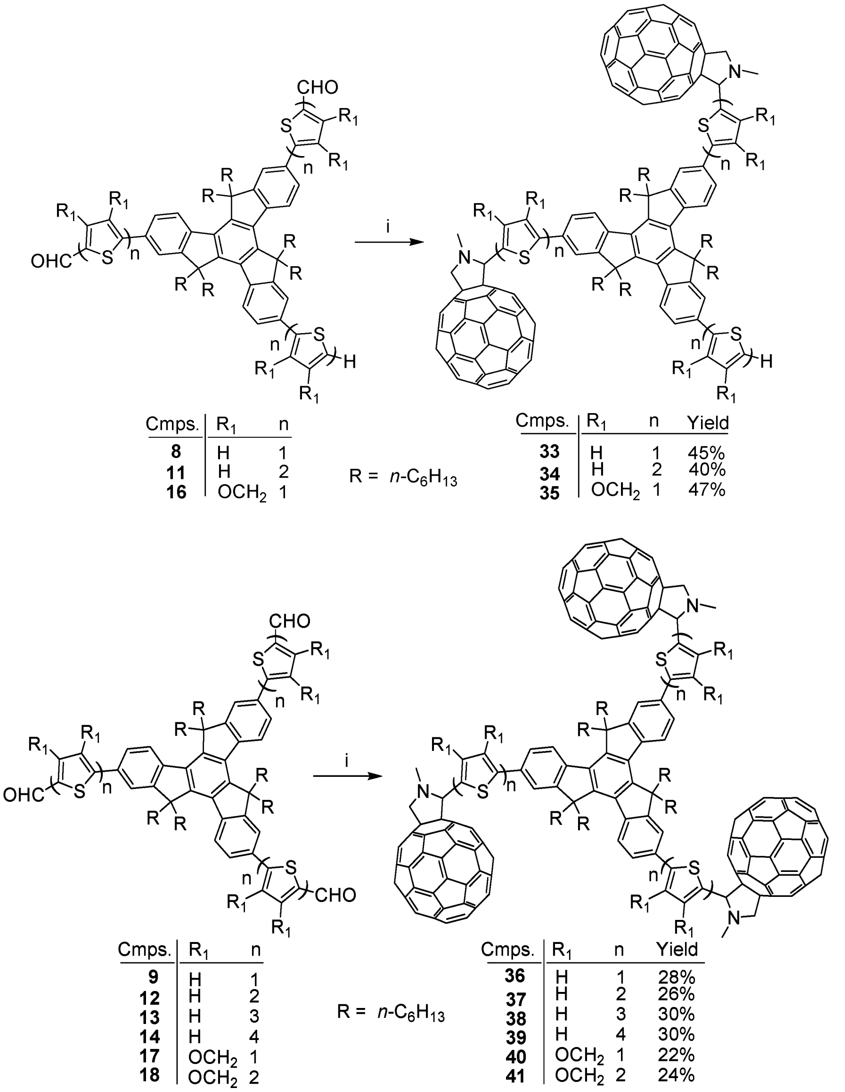
[15] See, for example: (a) Lambert, C.; Nöll, G.; Schämlzlin, E.; Meerholz, K.; Bräuchle, C. *Chem.*—*Eur. J.* **1998**, *4*, 2129−2134. (b) de Frutos, Ó.; Gómez-Lor, B.; Granier, T.; Jiménez-Barbero, J.; Monge, M. Á.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 204−207. (c) Gómez-Lor, B.; de Frutos, Ó.; Ceballos, P. A.; Granier, T.; Echavarren, A. M. *Eur. J. Org. Chem.* **2001**, 2107−2114. (d) de Frutos, Ó.; Granier, T.; Gómez-Lor, B.; Jiménez-Barbero, J.; Monge, M. Á.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Chem.*—*Eur. J.* **2002**, *8*, 2879−2890.

[16] (a) Kagan, J.; Arora, S. K. *J. Org. Chem.* **1983**, *48*, 4317−4320. (b) Han, E. M.; Do, L. M.; Niidome, Y.; Fujihira, M. *Chem. Lett.* **1994**, 969−970.

[17] See, for example: ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887−5889.

SCHEME 11 [a]



Cmps.	R_1	n
8	H	1
11	H	2
16	OCH_2	1

R = n-C_6H_{13}

Cmps.	R_1	n	Yield
33	H	1	45%
34	H	2	40%
35	OCH_2	1	47%

Cmps.	R_1	n
9	H	1
12	H	2
13	H	3
14	H	4
17	OCH_2	1
18	OCH_2	2

R = n-C_6H_{13}

Cmps.	R_1	n	Yield
36	H	1	28%
37	H	2	26%
38	H	3	30%
39	H	4	30%
40	OCH_2	1	22%
41	OCH_2	2	24%

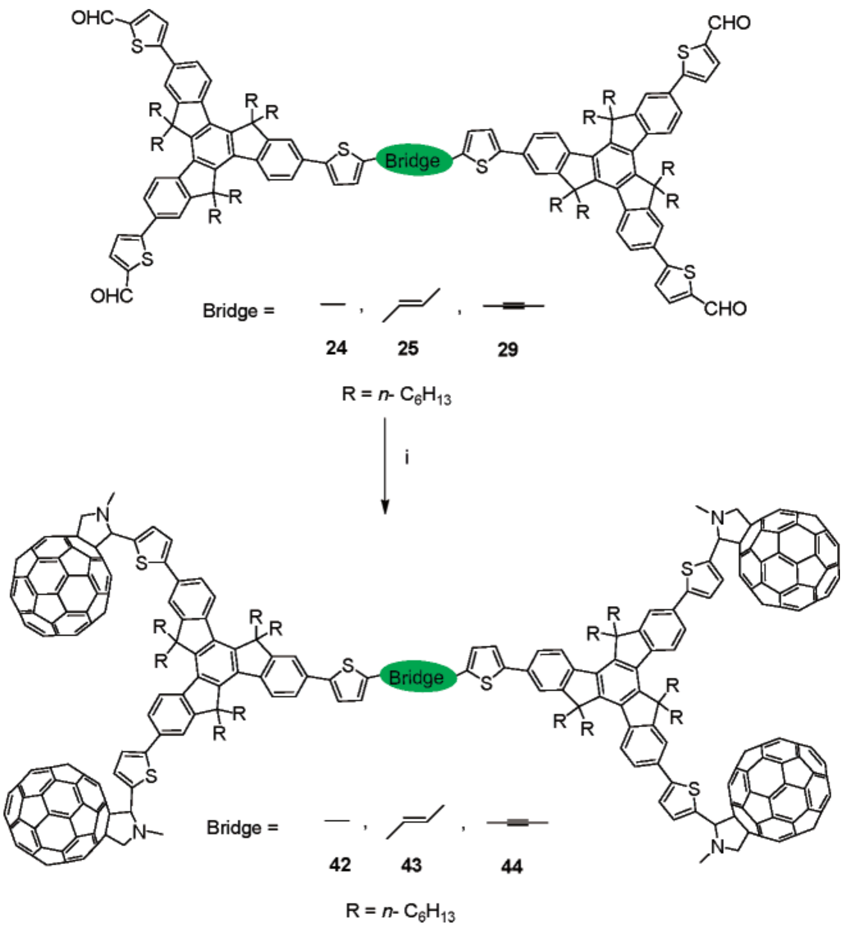
[a] Reagents and conditions: (i) *N*-methylglycine, C_{60}, chlorobenzene, reflux, 12 h.

the maximum peak of **5** only slightly red-shifted in comparison with that of **1**, the maximum emission peak of **6** red-shifted about 13 nm in comparison with **2**. Moreover, the results all demonstrated that the emission spectra of truxene derivatives were liable to be tuned by introducing oligothiophene segments.

Figure 4 compares the absorption spectra of **2**, **31**, **34**, and **37** in dilute dichlorobenzene solutions; for this series, they owned the same bridge (bithiophene) and contained different numbers of C_{60}: one C_{60} moiety for **31**, two C_{60} moieties for **34**, and three C_{60} moieties for **37**. Not only did we observe that the absorption $\lambda_{\max}$ at about 383 nm for **2** slightly red-shifted with the increase in the content of C_{60}, but we also found the characteristic absorption of C_{60} at around 330 nm in all spectra enhanced with an increase in the content of the C_{60} moieties. For another series all bearing three C_{60} moieties, **36**, **37**, and **38** as well as **39**, we observed another characteristic absorption of C_{60} at around 430 nm in the absorption spectrum of **36**. We observed obvious red-shift from about 350 nm to 440 nm with the increase in the conjugation length of the oligothiophenes from the dyads **36**, **37**, and **38** to **39**, and then the C_{60} absorption peaks were extinguished in the broad peak due to the predomination of the strong absorption of the oligothiophenes in this region (as shown in Figure 5). The absorption behaviors of other C_{60} dyads also exhibited similar features. Furthermore, all C_{60} adducts also exhibited a broad, weak absorption peak at about 705 nm. Finally, we observed that the inductive electron-releasing effect of the fulleropyrrolidine group caused a slight red-shift of $\lambda_{\max}$ (per C_{60} group, red-shift of about 4 nm); for instance, for **39**, the absorption peak red-shifted 11 nm in comparison with that of **4**. The results demonstrated that in the ground state there was no significant intramolecular electronic communication or charge-transfer interaction between the fullerenes and the hosts through the pyrrolidine segments.

We observed that the obvious intramolecular and intermolecular singlet energy transfer from a photoexcited π-conjugated oligomer to a covalently bonded C_{60} moiety happened in the excited states for all C_{60} adducts. Figure 6 compares the effect of both the content of C_{60} and the length of the bridge on the emission spectra in dilute solutions. When excited at the wavelength of maximum absorption of the oligomers, the fluorescence of C_{60} dyads in 1,2-dichlorobenzene solutions was strongly quenched by 4 orders of magnitude with respect to the emissions of **1**−**6**. The emission quenching in solution also confirmed unambiguously the covalent linkage of the C_{60}

SCHEME 12 [a]



[a] Reagents and conditions: (i) *N*-methylglycine, C_{60}, chlorobenzene, reflux, 12 h, 34% for **42**, 30% for **43**, and 35% for **44**.

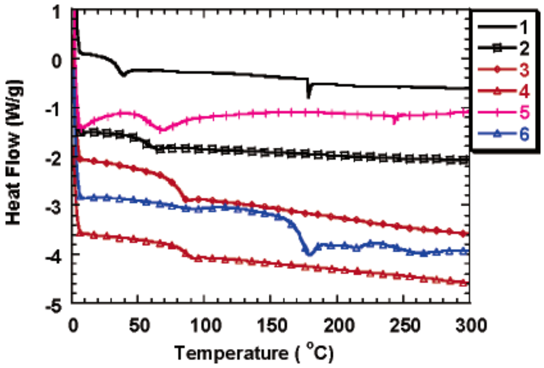


FIGURE 1. DSC curves (second run) of **1**−**6**.

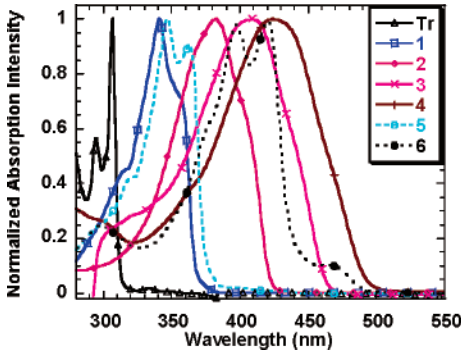


FIGURE 2. Normalized absorption spectra of **1**−**6** in dilute THF solutions.

moieties to the oligothiophenes. Such quenching was consistent with a fast decay of the oligothiophene-functionalized truxene derivative (S1) states via intramolecular singlet energy transfer from a photoexcited π-conjugated oligomer to a covalently bonded fullerene moiety. Such fast singlet energy transfer produced the singlet excited state of the fullerene moiety, similar to direct photoexcitation. The emission intensity of **5** decreased dramatically when the number of C_{60} moieties increased from 1 to 3, which also indicated that the content of the C_{60} moiety also played a key role in intramolecular energy transfer from the photoexcited conjugated oligomers to the C_{60} moieties. The comparison of the emission quenching of **36**, **37**, **38**, and **39** (as illustrated in Figure 7) also indicated that the intramolecular energy transfer distinctly depended on the oligothiophene bridge length, in other words, the distance between the two chromophores.[18]

Figure 8 illustrates the absorption spectra of **22**, **23**, and **27** in dilute THF solutions, which exhibited the same characteristic maximum absorption as chromophore **1** (at about 342 nm).[8a,f] Another absorption peaked at 413 nm for **22**, and at 443 nm for **23** as well as at 394 nm for **27**, which red-shifted as a result of the increased conjugation length of branches, respectively. In comparison with other thiophene derivatives with similar

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[18] Giacalone, F.; Segura, J. L.; Martin, N.; Guldi, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 5340−5341.

TABLE 1. Molecular Weights, T_g, and Optical Properties of New Compounds in Dilute Solutions

compd.	M_W	abs. λ_{max} nm in soln.	PL λ_{max} nm in soln.	T_g (0 °C)
1	1093	341	365, 383	32
2	1340	383	406, 431	53
3	1586	411	448, 478	77
4	1832	424	475, 512	78
5	1266	347, 363	370, 388	54
6	1687	398, 420	419, 445	175
22	2185	342, 354, 413	455, 488	
23	2211	342, 354, 443	477, 510	
27	2209	342, 354, 394	443, 470	
30	1868	343, 706	420	
31	2116	386, 705	414, 438	
32	2041	350, 432, 707	437	
33	2645	346, 706	418	
34	2891	390, 705	436	
35	2819	358, 432, 707	425	
36	3421	353, 706	383	
38	3913	418, 705	508	
39	4160	435, 705	515	
37	3667	395, 705	433	
40	3595	360, 432, 707	422	
41	4015	411, 435, 707	456	
42	5287	341, 355, 433	460	
43	5313	341, 355, 433	483	
44	5311	341, 355, 433	446	

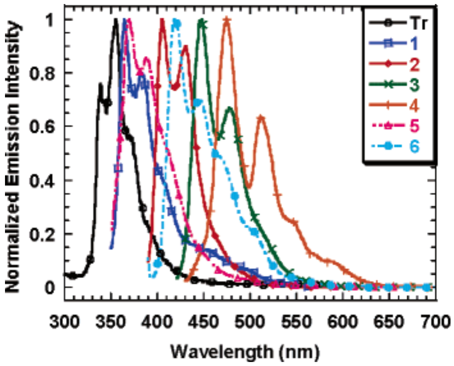

FIGURE 3. Normalized emission spectra of **1**−**6** in dilute THF solutions.

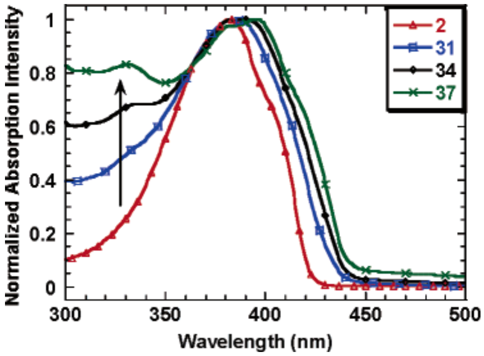

FIGURE 4. Comparison of the absorption spectra of **2**, **31**, **34**, and **37**.

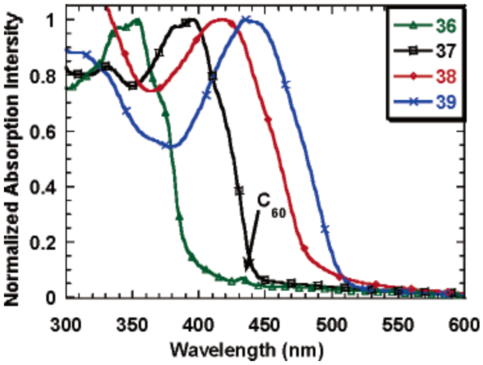

FIGURE 5. Comparison of the absorption spectra of **36**, **37**, **38**, and **39**.

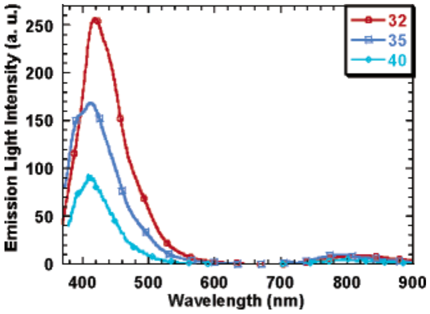

FIGURE 6. Comparison of the emission spectra of **32**, **35**, and **40** in 1,2-dichlorobenzene solution. Absorption intensities of the samples (A = 0.2) were matched at the excitation wavelength.

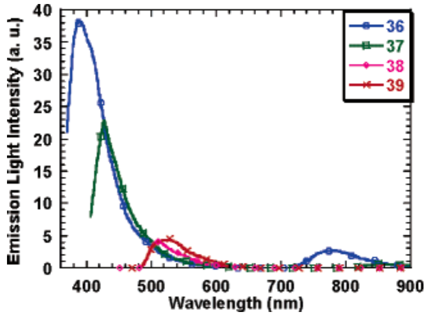

FIGURE 7. Comparison of the emission spectra of **36**, **37**, **38**, and **39** in 1,2-dichlorobenzene solution. Absorption intensities of samples (A = 0.2) were matched at the excitation.

structures, for example **FT2** (404 nm),[19] the absorption maximum of **22** red-shifted about 9 nm as a result of increasing the effective conjugation length. In comparison with **22** (413 nm), a more effective conjugation length along the molecule as a result of the inserting of the vinylene unit achieved the red-shift (30 nm) for **23**; however, the poor conjugation between two thiophene-functionalized truxene chromophores linked by ethynylene spacers blue-shifted 19 nm for **27**.

For PL spectra in THF solution, **22**, **23**, and **27** exhibited well-defined structured behaviors. We did not observe the same emission as that of **1** (see the Supporting Information), which indicated that the intramolecular energy transfer happened within **22**, **23**, and **27**. The maximum emission peaks red-shifted about 91 nm for **22**, 113 nm for **23**, and 79 nm for **27** compared to that of **1**.

Figure 9 compares the absorption and emission spectra of C_{60} dyads **42**, **43**, and **44** in dilute dichlorobenzene solution. All absorption spectra exhibited a characteristic peak at about 355 nm. It's interesting that the intensity of another characteristic absorption for all three compounds at around 390−440 nm was decreased compared with those of compounds **22**, **23**, and **27**.

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[19] Wong, K.-T.; Wang, C.-F.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *Org. Lett.* **2002**, *4*, 4439.

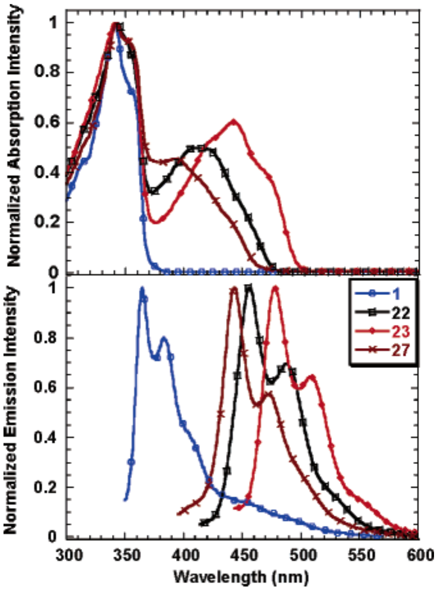

FIGURE 8. Normalized absorbance spectra and emission spectra of **1**, **22**, **23**, and **27**, recorded in dilute THF solutions at room temperature.

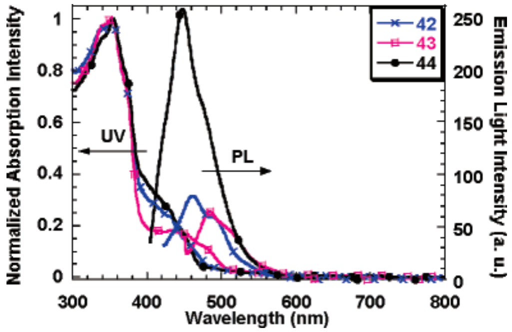

FIGURE 9. Normalized absorbance spectra and emission spectra of **42**, **43**, and **44**, recorded in dilute solutions at room temperature.

All C_{60} adducts also exhibited the broad, weak absorption peak at about 705 nm. The results demonstrated that in the ground state there was no significant intramolecular electronic communication or charge-transfer interaction between C_{60} and the hosts through the pyrrolidine segment.

When excited at the wavelength of maximum absorption of these oligomers, the fluorescence of the C_{60} dyads in 1,2-dichlorobenzene solutions was strongly quenched with respect to the emission of the oligomers. Unlike the UV−vis spectra, emission spectra showed interaction in the excited state for these dyads. We observed that the intramolecular and intermolecular singlet energy transfers from a photoexcited conjugated oligomer to a C_{60} moiety happened in the excited state for all C_{60} adducts.[20] The emission intensity of the oligomer decreased dramatically from triple- and single-bonds to double-bonds. At the same absorbance for these compounds, the quenching of the emission of **42** and **43** was more obvious than that of **44**. The results also indicated that the spacers also played a key role in intramolecular energy transfer from the photoexcited conjugated oligomers to the C_{60} moieties.

In conclusion, we have successfully developed an effective approach to a series of star-shaped oligothiophene-functionalized truxene derivatives and their corresponding [60]fullerene adducts. Such adducts bear one to four chromophores including the truxene moiety as the core and oligothiophenes as the bridge as well as the C_{60} as the end-capping groups. The direction character of our synthetic approaches efficiently offers us the desired compounds with different bridge lengths for easy tuning of the absorption and emission behaviors and affords four kinds of C_{60} derivatives bearing one, two, three, and four pyrrolidinofullerene moieties, which provide us a way to investigate the relationship of the structure and the properties of such materials. The hexyl substituents efficiently reduce the π-stacking of all compounds, both in solutions and in films. All compounds exhibit good thermal stability. The absorption and emission spectra of the oligothiophene-functionalized truxene derivatives are liable to be tuned by the π-linkages. The investigation of photophysical properties of new C_{60} adducts demonstrates that the significant photoinduced intramolecular electronic communication and intermolecular charge transfer between the hosts and *N*-methylfulleropyrrolidine moieties in the excited states have been formed, although no such interactions happen in the ground state. Further experiments to understand the details about the energy transfer and to fabricate the solar cell devices are still in progress in our laboratory.

Experimental Section

General Procedure for Monoaldehydes to the C_{60}-Functionalized Dyads. A mixture of C_{60} (150 mg, 0.23 mmol), monoaldehyde (0.115 mmol), and *N*-methylglycine (82 mg, 0.92 mmol) was refluxed for 10 h in degassed anhydrous chlorobenzene under an inert atmosphere. After solvent removal, the residue was purified over silica gel to gave a black solid.

Compound 30. The general procedure for the preparation of C_{60}-functionalized dyads from monoaldehydes was followed to give **30** in 55% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.34−8.36 (d, J = 8.4 Hz, 3H, Ar−H), 7.68−7.74 (d, s, J = 8.4 Hz, 6H, Ar−H), 7.46−7.47 (m, 4H, Th−H), 7.32−7.33 (d, J = 4.8 Hz, 2H, Th−H), 7.13−7.19 (dd, J = 4.8 Hz, J = 3.6 Hz, 2H, Th−H), 5.30 (s, 1H, C−H), 5.01−5.04 (d, J = 9.3 Hz, 1H, CH_2), 4.28−4.32 (d, J = 9.3 Hz, 1H, CH_2), 3.02 (s, 3H, *N*-CH_3), 2.95 (m, 6H, CH_2), 2.15 (m, 6H, CH_2), 0.86−0.92 (m, 36H, CH_2), 0.60−0.64 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 155.64, 154.05, 153.59, 152.83, 147.14, 146.71, 146.06, 145.78, 145.27, 145.10, 144.70, 144.56, 144.22, 142.93, 142.47, 141.92, 141.51, 140.09, 139.81, 139.55, 139.18, 137.73, 173.03, 136.64, 135.75, 135.52, 132.75, 132.37, 128.85, 128.00, 124.70, 124.20, 124.06, 122.93, 122.31, 119.26, 118.87, 79.26, 76.95, 69.91, 63.51, 55.42, 40.34, 37.12, 31.75, 29.78, 24.13, 22.74, 14.57. MALDI-TOF-MS: *m*/*z* 1868.7 (M^+).

Compound 31. The general procedure for the preparation of C_{60}-functionalized dyads from monoaldehydes was followed to give **31** in 50% yield. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz, ppm, δ): 8.32−8.34 (d, J = 8.4 Hz, 3H, Ar−H), 7.64 (d, s, J = 8.4 Hz, 6H, Ar−H), 7.31−7.33 (m, 4H, Th−H), 7.16−7.22 (m, 8H, Th−H), 7.00−7.03 (dd, J = 4.8 Hz, J = 3.6 Hz, 2H, Th−H), 5.24 (s, 3H, C−H), 4.95−4.98 (d, J = 9.3 Hz, 1H, CH_2), 4.23−4.26 (d, J = 9.3 Hz, 1H, CH_2), 2.90−2.96 (s, m, *N*-CH_3, 9H, CH_2), 2.09 (m, 6H, CH_2), 0.86−0.92 (m, 36H, CH_2), 0.60−0.64 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3/CS_2$, 75 MHz, ppm): δ 155.57, 154.25, 153.60, 152.83, 152.79, 147.14, 146.63, 146.19, 146.14, 146.10, 146.05, 145.97, 145.79, 145.61, 145.49, 145.42, 145.32, 145.22, 145.16, 145.12, 145.09, 145.01, 144.96, 144.55, 144.49, 144.21, 143.74, 143.42, 143.01, 142.85, 142.55, 142.44, 142.13, 142.00, 141.91, 141.85, 141.79, 141.53, 141.48, 140.05, 139.86, 139.7, 139.65,

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[20] Langa, F.; Gomez-Escalonilla, M. J.; Rueff, J.-M.; Duarte, T. M. F.; Nierengarten, J.-F.; Palermo, V.; Samor, P.; Rio, Y.; Accorsi, G.; Armaroli, N. *Chem.*−*Eur. J.* **2005**, *11*, 4405−4415.

139.55, 138.76, 137.77, 137.44, 137.02, 136.52, 136.35, 135.77, 135.47, 132.15, 132.05, 128.69, 127.76, 124.58, 124.24, 123.79, 123.47, 122.64, 118.87, 79.21, 76.88, 69.92, 68.63, 55.63, 40.40, 37.11, 31.58, 29.62, 24.05, 22.44, 14.02. MALDI-TOF-MS: *m/z* 2114.7 (M$^+$).

Compound 32. The general procedure for the preparation of C$_{60}$-functionalized dyads from monoaldehydes was followed to give **32** in 51% yield. ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ 8.33−8.36 (d, J = 8.4 Hz, 3H, Ar−H), 7.82−7.83 (d, J = 3.6 Hz, 3H, Ar−H), 7.76 (s, 3H, Ar−H), 6.34 (s, 2H, Th−H), 5.53 (s, 1H, C−H), 5.01−5.04 (d, J = 9.3 Hz, 1H, CH$_2$), 4.30−4.40 (m, 13H, OCH$_2$-CH$_2$O, CH$_2$), 3.02 (s, 3H, *N*-CH$_3$), 2.95 (m, 6H, CH$_2$), 2.15 (m, 6H, CH$_2$), 0.86−0.92 (m, 36H, CH$_2$), 0.60−0.64 (m, 30H, CH$_2$, CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 156.10, 154.18, 154.05, 153.80, 153.26, 147.27, 146.74, 146.45, 146.37, 146.27, 146.14, 146.04, 145.90, 145.80, 145.50, 145.38, 145.30, 145.24, 145.13, 144.84, 144.61, 144.33, 143.09, 142.94, 142.59, 142.53, 142.33, 142.11, 142.00, 141.89, 141.64, 140.12, 139.86, 139.74, 139.07, 138.84, 138.08, 138.00, 137.89, 137.24, 136.67, 135.82, 135.51, 131.13, 130.82, 124.64, 123.91, 119.33, 118.10, 97.20, 69.90, 68.92, 65.01, 64.83, 64.64, 64.45, 55.64, 40.61, 37.03, 31.51, 29.52, 23.98, 22.29, 13.89. MALDI-TOF-MS: *m/z* 2041.7 (M$^+$).

General Procedure for Dialdehydes to the C$_{60}$-Functionalized Dyads. A mixture of C$_{60}$ (64 mg, 0.092 mmol), dialdehyde (0.022 mmol), and *N*-methylglycine (32.8 mg, 0.37 mmol) was refluxed for 10 h in degassed anhydrous chlorobenzene under an inert atmosphere. After solvent removal, the residue was purified over silica gel to gave black solids.

Compound 33. The general procedure for the preparation of C$_{60}$-functionalized dyads from dialdehydes was followed to give **33** in 45% yield. ^{1}H NMR (CDCl$_3$/CS$_2$, 300 MHz, ppm): δ 8.31−8.34 (d, J = 8.4 Hz, 3H, Ar−H), 7.64−7.67 (d, s, J = 8.4 Hz, 6H, Ar−H), 7.40−7.44 (m, 5H, Th−H), 7.29−7.31 (d, J = 3.6 Hz, 1H, Th−H), 7.11−7.14 (dd, J = 4.8 Hz, J = 3.6 Hz, 1H, Th−H), 5.30 (s, 2H, C−H), 5.02−5.05 (d, J = 9.3 Hz, 2H, CH$_2$), 4.28−4.31 (d, J = 9.3 Hz, 2H, CH$_2$), 2.92−2.99 (s, m, 12H, *N*-CH$_3$, CH$_2$), 2.15 (m, 6H, CH$_2$), 0.86−0.92 (m, 36H, CH$_2$), 0.60−0.64 (m, 30H, CH$_2$, CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 155.66, 154.22, 154.13, 153.68, 153.00, 152.93, 147.17, 146.73, 146.26, 146.22, 146.15, 146.09, 146.05, 146.01, 145.96, 145.81, 145.66, 145.51, 145.46, 15.36, 145.32, 145.26, 145.20, 145.12, 145.04, 144.95, 144.67, 144.58, 144.53, 144.24, 143.02, 142.87, 142.57, 142.47, 142.17, 142.07, 142.03, 141.94, 141.85, 141.56, 141.51, 140.08, 139.88, 139.73, 139.67, 139.68, 139.35, 137.81, 137.71, 137.02, 136.57, 135.75, 135.51, 132.56, 132.23, 128.98, 127.93, 124.77, 124.52, 124.11, 123.93, 122.83, 122.18, 119.22, 118.86, 79.40, 77.00, 69.94, 68.61, 55.55, 40.34, 37.04, 31.53, 29.77, 23.99, 22.41, 14.18. MALDI-TOF-MS: *m/z* 2645.2 (M$^+$).

Compound 34. The general procedure for the preparation of C$_{60}$-functionalized dyads from dialdehydes was followed to give **34** in 40% yield. ^{1}H NMR (CDCl$_3$/CS$_2$, 300 MHz, ppm): δ 8.29−8.32 (d, J = 8.4 Hz, 3H, Ar−H), 7.54−7.63 (d, s, J = 8.4 Hz, 6H, Ar−H), 7.31−7.34 (m, 4H, Th−H), 7.19−7.24 (m, 8H, Th−H), 7.01−7.03 (dd, J = 4.8 Hz, J = 3.6 Hz, 1H, Th−H), 5.24 (s, 3H, C−H), 4.97−5.00 (d, J = 9.3 Hz, 2H, CH$_2$), 4.24−4.28 (d, J = 9.3 Hz, 2H, CH$_2$), 2.90−2.96 (s, m, 12H, *N*-CH$_3$, CH$_2$), 2.09 (m, 6H, CH$_2$), 0.86−0.92 (m, 36H, CH$_2$), 0.60−0.64 (m, 30H, CH$_2$, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$, 75 MHz, ppm): δ 155.63, 154.26, 153.65, 152.89, 152.81, 147.20, 146.67, 146.24, 146.19, 146.12, 145.97, 145.83, 145.66, 145.54, 145.46, 145.36, 145.27, 145.13, 145.06, 144.59, 144.55, 144.25, 143.79, 143.47, 143.05, 142.60, 142.49, 142.17, 142.04, 141.96, 141.89, 141.83, 141.56, 140.10, 139.90, 139.74, 139.65, 138.81, 137.77, 137.49, 137.04, 136.54, 136.37, 135.77, 135.49, 132.22, 132.11, 128.70, 127.77, 124.81, 124.60, 124.27, 123.82, 123.61, 123.52, 122.67, 118.95, 79.28, 77.00, 69.92, 68.60, 55.58, 40.31, 37.06, 31.53, 29.78, 23.99, 22.41, 13.94. MALDI-TOF-MS: *m/z* 2891 (M$^+$).

Compound 35. The general procedure for the preparation of C$_{60}$-functionalized dyads from dialdehydes was followed to give **35** in 47% yield. ^{1}H NMR (CDCl$_3$/CS$_2$, 300 MHz, ppm): δ 8.30−8.33 (d, J = 8.4 Hz, 3H, Ar−H), 7.73−7.83 (d, s, J = 8.4 Hz, 6H, Ar−H), 6.33 (s, 1H, Th−H), 5.51 (s, 2H, C−H), 5.00−5.04 (d, J = 9.3 Hz, 2H, CH$_2$), 4.26−4.38 (m, 14H, OCH$_2$CH$_2$O, CH$_2$), 3.01 (s, 6H, *N*-CH$_3$), 2.90 (m, 6H, CH$_2$), 2.11 (m, 6H, CH$_2$), 0.86−0.92 (m, 36H, CH$_2$), 0.60−0.64 (m, 30H, CH$_2$, CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 156.14, 153.85, 153.28, 147.33, 146.78, 146.35, 146.18, 145.95, 145.85, 145.56, 145.30, 145.19, 144.66, 144.37, 143.15, 142.97, 142.59, 142.32, 142.16, 141.92, 141.69, 140.17, 139.80, 139.09, 138.12, 137.27, 136.69, 135.83, 135.55, 131.15, 124.71, 123.97, 119.44, 97.30, 69.97, 68.96, 65.05, 64.68, 55.69, 40.63, 37.00, 31.45, 29.69, 24.01, 22.68, 22.32, 14.11, 13.93. MALDI-TOF-MS: *m/z* 2819 (M$^+$).

General Procedure for Trialdehydes to the C$_{60}$-Functionalized Dyads. A mixture of C$_{60}$ (95 mg, 0.132 mmol), trialdehyde(0.022 mmol), and *N*-methylglycine (47.0 mg, 0.528 mmol) was refluxed for 10 h in degassed anhydrous chlorobenzene under an inert atmosphere. After solvent removal, the residue was purified over silica gel to give dark brown solids.

Compound 36. The general procedure for the preparation of C$_{60}$-functionalized dyads from trialdehydes was followed to give **36** in 28% yield. ^{1}H NMR (CDCl$_3$/CS$_2$, 300 MHz, ppm): δ 8.26−8.29 (d, J = 8.4 Hz, 3H, Ar−H), 7.60−7.63 (d, s, J = 8.4 Hz, 6H, Ar−H), 7.40−7.41 (d, J = 3.6 Hz, 3H, Th−H), 7.35−7.36 (d, J = 3.6 Hz, 3H, Th−H), 5.28 (s, 3H, C−H), 5.00−5.03 (d, J = 9.3 Hz, 3H, CH$_2$), 4.27−4.30 (d, J = 9.3 Hz, 3H, CH$_2$), 2.89−2.98 (s, m, 15H, *N*-CH$_3$, CH$_2$), 2.08 (m, 6H, CH$_2$), 0.86−0.92 (m, 36H, CH$_2$), 0.60−0.64 (m, 30H, CH$_2$, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$, 75 MHz, ppm): δ 155.74, 154.29, 153.77, 153.08, 153.01, 147.24, 146.79, 146.28, 146.21, 146.11, 145.87, 145.73, 145.56, 145.51, 145.43, 145.27, 145.18, 145.11, 144.64, 144.58, 144.30, 143.09, 143.02, 142.93, 142.64, 142.53, 142.22, 142.10, 142.00, 141.91, 141.62, 141.56, 140.14, 139.93, 139.74, 137.81, 137.08, 136.61, 135.80, 135.55, 132.29, 129.07, 124.84, 123.96, 122.22, 120.42, 118.92, 79.49, 77.21, 70.00, 68.70, 55.64, 40.38, 37.07, 31.55, 29.59, 24.05, 22.41, 13.95. MALDI-TOF-MS: *m/z* 3420 (M$^+$).

Compound 37. The general procedure for the preparation of C$_{60}$-functionalized dyads from trialdehydes was followed to give **37** in 26% yield. ^{1}H NMR (CDCl$_3$/CS$_2$, 300 MHz, ppm): δ 8.28−8.31 (d, J = 8.4 Hz, 3H, Ar−H), 7.60−7.62 (d, s, J = 8.4 Hz, 6H, Ar−H), 7.30−7.33 (d, d, J = 3.6 Hz, 6H, Th−H), 7.18−7.19 (d, J = 3.6 Hz, 3H, Th−H), 7.14−7.16 (d, J = 3.6 Hz, 3 H, Th−H), 5.24 (s, 3H, C−H), 5.00−5.01 (d, J = 9.3 Hz, 3H, CH$_2$), 4.25−4.28 (d, J = 9.3 Hz, 3H, CH$_2$), 2.90−2.96 (s, m, *N*-CH$_3$, 15H, CH$_2$), 2.09 (m, 6H, CH$_2$), 0.86−0.92 (m, 36H, CH$_2$), 0.60−0.64 (m, 30H, CH$_2$, CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 155.57, 154.18, 153.58, 152.83, 152.72, 147.14, 146.62, 146.19, 146.13, 146.06, 145.97, 145.93, 145.78, 145.61, 145.49, 145.42, 145.30, 145.23, 145.09, 145.01, 144.93, 144.55, 144.20, 143.72, 143.00, 142.84, 142.55, 142.44, 142.12, 142.00, 141.91, 141.84, 141.78, 141.52, 140.05, 139.86, 139.69, 139.61, 139.54, 138.76, 137.71, 137.00, 136.51, 136.35, 135.43, 132.10, 128.62, 124.74, 123.80, 123.57, 122.64, 118.91, 79.22, 76.88, 69, 88, 68.54, 55.51, 40.26, 37.03, 31.52, 29.55, 23.99, 22.43, 13.94. MALDI-TOF-MS: *m/z* 3667 (M$^+$).

Compound 38. The general procedure for the preparation of C$_{60}$-functionalized dyads from trialdehydes was followed to give **38** in 30% yield. ^{1}H NMR (CS$_2$/CDCl$_3$, 300 MHz, ppm): δ 8.26−8.29 (d, J = 8.4 Hz, 3H, Ar−H), 7.57−7.58 (s, d, J = 8.4 Hz, 6H, Ar−H), 7.06−7.29 (m, 18H, Th−H), 5.21 (s, 3H, C−H), 4.94−4.97 (d, J = 9.3 Hz, 3H, CH$_2$), 4.22−4.25 (d, J = 9.3 Hz, 3H, CH$_2$), 2.93−2.95 (m, CH$_2$, 15H, *N*-CH$_3$), 2.15 (m, 6H, CH$_2$), 0.86−0.92 (m, 36H, CH$_2$), 0.60−0.64 (m, 30H, CH$_2$, CH$_3$). ^{13}C NMR (CS$_2$/CDCl$_3$, 75 MHz, ppm): δ 155.60, 154.27, 153.62, 152.84, 152.73, 147.19, 146.64, 146.09, 145.82, 145.64, 145.53, 145.35, 145.13, 144.58, 144.25, 143.74, 143.04, 142.88, 142.60, 142.48, 142.15, 142.03, 141.95, 141.81, 141.56, 140.09, 139.89, 139.73, 138.38, 137.78, 137.04, 136.50, 136.02, 135.76, 135.46, 132.09, 128.89, 128.69, 128.19, 125.21, 124.84, 124.67, 124.49, 124.12, 123.66, 122.800, 118.91, 115.62, 79.25, 77.00, 69.90, 68.58, 55.58, 40.29, 37.07, 32.02, 30.17, 24.02, 22.85, 13.94. MALDI-TOF-MS: *m*/*z* 3913 (M^+).

Compound 39. The general procedure for the preparation of C_{60}-functionalized dyads from trialdehydes was followed to give **39** in 30% yield. ^{1}H NMR ($CS_2/CDCl_3$, 300 MHz, ppm): δ 8.28−8.32 (d, J = 8.4 Hz, 3H, Ar−H), 7.59−7.61 (s, d, J = 8.4 Hz, 6H, Ar−H), 7.04−7.29 (m, 24H, Th−H), 5.22 (s, 3H, C−H), 4.96−4.99 (d, J = 9.3 Hz, 3H, CH_2), 4.23−4.26 (d, J = 9.3 Hz, 3H, CH_2), 2.93−2.95 (m, 15H, CH_2, *N*-CH_3), 2.11−2.15 (m, 6H, CH_2), 0.86−0.92 (m, 36H, CH_2), 0.60−0.64 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CS_2/CDCl_3$, 75 MHz, ppm): δ 155.58, 154.26, 153.60, 152.81, 147.19, 146.62, 146.09, 145.82, 145.63, 145.33, 145.17, 145.13, 144.58, 144.23, 143.76, 143.03, 142.87, 142.47, 142.02, 141.94, 141.82, 141.52, 140.08, 139.95, 139.72, 138.27, 137.80, 137.03, 136.50, 136.21, 135.74, 135.45, 132.11, 129.36, 128.68, 124.67, 124.39, 124.25, 123.66, 122.86, 118.95, 79.23, 77.00, 69.90, 55.58, 40.27, 37.14, 32.00, 30.14, 24.02, 23.33, 13.94. MALDI-TOF-MS: *m*/*z* 4160 (M^+).

Compound 40. The general procedure for the preparation of C_{60}-functionalized dyads from trialdehydes was followed to give **40** in 22% yield. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz, ppm): δ 8.16−8.18 (d, J = 8.4 Hz, 3H, Ar−H), 7.61−7.671 (d, s, J = 8.4 Hz, 6H, Ar−H), 5.45 (s, 3H, C−H), 4.92−4.96 (d, J = 9.3 Hz, 3H, CH_2), 4.13−4.31 (d, d, J = 9.3 Hz, 15H, OCH_2CH_2O, CH_2), 2.96 (s, 9H, *N*-CH_3), 2.81 (m, 6H, CH_2), 2.04 (m, 6H, CH_2), 0.81−0.98 (m, 36H, CH_2), 0.47−0.58 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3/CS_2$, 75 MHz, ppm): δ 155.97, 153.85, 153.66, 153.07, 147.15, 146.62, 146.31, 146.23, 146.20, 146.12, 146.02, 145.97, 145.92, 145.79, 145.69, 145.44, 145.31, 145.25, 145.14, 145.11, 145.02, 144.72, 144.55, 144.50, 144.23, 142.98, 142.83, 142.52, 142.48, 142.45, 142.18, 142.06, 142.00, 141.91, 141.83, 141.52, 140.05, 140.01, 139.77, 139.64, 138.71, 137.79, 137,39, 137.12, 136.62, 135.66, 135.34, 130.91, 124.46, 124.02, 119.37, 118.37, 118.99, 111.75, 69.81, 68.76, 64.88, 64.53, 55.46, 40.45, 37.01, 31.59, 29.79, 24.02, 22.48, 14.01. MALDI-TOF-MS: *m*/*z* 3595 (M^+).

Compound 41. The general procedure for the preparation of C_{60}-functionalized dyads from trialdehydes was followed to give **41** in 24% yield. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz, ppm): δ 8.16−8.18 (d, J = 8.4 Hz, 3H, Ar−H), 7.59−7.66 (d, s, J = 8.4 Hz, 6H, Ar−H), 5.42 (s, 3H, C−H), 4.92−4.96 (d, J = 9.3 Hz, 3H, CH_2), 4.14−4.40 (m, 27H, OCH_2CH_2O, CH_2), 2.93 (s, 9H, *N*-CH_3), 2.82 (m, 6H, CH_2), 2.03 (m, 6H, CH_2), 0.81−0.98 (m, 36H, CH_2), 0.47−0.58 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 156.02, 154.68, 153.83, 153.65, 153.11, 147.16, 146.62, 146.25, 146.11, 146.04, 145.92, 145.80, 145.67, 145.44, 145.31, 145.15, 144.50, 144.25, 142.97, 142.83, 142.48, 142.02, 141.52, 140.05, 139.80, 139.65, 138.45, 137.85, 137.66, 137.50, 137.13, 136.64, 136.12, 135.66, 135.28, 131.10, 128.63, 124.45, 123.99, 119.07, 116.20, 108.10, 77.21, 69.96, 68.74, 65.13, 64.72, 55.46, 41.42, 40.55, 37.12, 32.83, 30.12, 23.99, 22.45, 13.97. MALDI-TOF-MS: *m*/*z* 4015 (M^+).

General Procedure for Tetraaldehydes to the C_{60}-Functionalized Dyads. A mixture of C_{60} (220 mg, 0.304 mmol), tetraaldehyde (0.038 mmol), and *N*-methylglycine (108 mg, 1.212 mmol) in degassed anhydrous chlorobenzene was refluxed for 10 h under inert atmosphere. After solvent removal, the residue was purified over silica gel to give dark brown solids.

Compound 42. The general procedure for the preparation of C_{60}-functionalized dyads from tetraaldehydes was followed to give **42** in 34% yield. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz, ppm): δ 8.37−8.39 (d, J = 8.4 Hz, 6H, Ar−H), 7.64−7.65 (d, s, 12H, Ar−H), 7.38−7.43 (d, J = 3.6 Hz, 8H, Th−H), 7.20−7.22 (d, J = 3.6 Hz, 2H, Th−H), 7.13−7.15 (d, J = 3.6 Hz, 2H, Th−H), 5.28 (s, 4H, C−H), 5.00−5.04 (d, J = 9.3 Hz, 4H, CH_2), 4.27−4.31 (d, J = 9.3 Hz, 4H, CH_2), 2.95−2.98 (s, m, 24H, CH_2, *N*-CH_3), 2.15−2.19 (m, 12H, CH_2), 0.90 (m, 72H, CH_2), 0.49−0.63 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CS_2/CDCl_3$, 75 MHz, ppm): δ 155.59, 154.17, 153.62, 152.93, 152.86, 147.12, 146.68, 146.18, 146.10, 146.03, 146.01, 145.96, 145.91, 145.76, 145.62, 145.47, 145.47, 145.42, 145.31, 145.28, 145.22, 145.16, 145.07, 144.99, 144.54, 144.48, 144.19, 143.35, 142.98, 142.83, 142.53, 142.43, 142.11, 141.98, 141.89, 141.79, 141.52, 141.46, 140.03, 139.84, 139.70, 139.58, 137.69, 136.99, 136.52, 135.72, 135.47, 132.19, 130.56, 128.96, 128.85, 128.58, 128.48, 128.07, 127.31, 126.27, 126.21, 125.16, 124.78, 123.90, 122.17, 79.32, 76.88, 69.88, 68.54, 37.74, 55.51, 40.37, 37.37, 37.09, 31.98, 30.11, 24.01, 22.84, 14.22, 14.01. MALDI-TOF-MS: *m*/*z* 5287 (M^+).

Compound 43. The general procedure for the preparation of C_{60}-functionalized dyads from tetraaldehydes was followed to give **43** in 30% yield. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz, ppm): δ 8.27−8.28 (d, J = 8.4 Hz, 6H, Ar−H), 7.63−7.64 (d, s, 12H, Ar−H), 7.40−7.41 (d, J = 3.6 Hz, 4H, Th−H), 7.35−7.37 (d, J = 3.6 Hz, 4H, Th−H), 7.30−7.32 (d, J = 3.6 Hz, 2H, Th−H), 7.05−7.08 (d, s, J = 3.6 Hz, 4H, Th−H, double bond-H), 5.28 (s, 4H, C−H), 5.00−5.04 (d, J = 9.3 Hz, 4H, CH_2), 4.27−4.31 (d, J = 9.3 Hz, 4H, CH_2), 2.95−2.98 (s, m, 24H, CH_2, *N*-CH_3), 2.15−2.19 (m, 24H, CH_2), 0.90 (m, 72H, CH_2), 0.49−0.63 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CS_2/CDCl_3$, 75 MHz, ppm): δ 155.67, 154.21, 135.68, 153.00, 152.92, 147.17, 146.73, 146.25, 146.14, 146.09, 146.05, 146.00, 145.96, 145.81, 145.66, 145.52, 145.46, 145.36, 145.20, 145.12, 145.04, 144.98, 144.58, 144.24, 143.47, 143.03, 142.88, 142.58, 142.48, 142.16, 142.03, 141.94, 141.86, 141.56, 141.51, 140.09, 139.88, 139.73, 139.64, 137.74, 137.02, 136.56, 135.74, 135.50, 132.29, 128.97, 128.17, 127.37, 124.78, 123.95, 123.54, 122.21, 121.35, 118.91, 79.42, 77.21, 69.95, 68.61, 55.56, 40.33, 37.44, 31.56, 29.80, 24.03, 22.45, 13.98. MALDI-TOF-MS: *m*/*z* 5313 (M^+).

Compound 44. The general procedure for the preparation of C_{60}-functionalized dyads from tetraaldehydes was followed to give **44** in 35% yield. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz, ppm): δ 8.31−8.33 (d, J = 8.4 Hz, 6H, Ar−H), 7.64−7.65 (d, s, 12H, Ar−H), 7.40−7.43 (d, J = 3.6 Hz, 4H, Th−H), 7.35−7.36 (d, J = 3.6 Hz, 4H, Th−H), 7.35−7.37 (d, J = 3.6 Hz, 2H, Th−H), 7.31−7.31 (d, J = 3.6 Hz, 2H, Th−H), 5.28 (s, 4H, C−H), 5.00−5.04 (d, J = 9.3 Hz, 4H, CH_2), 4.27−4.31 (d, J = 9.3 Hz, 4H, CH_2), 2.95−2.98 (s, m, 24H, CH_2, *N*-CH_3), 2.15−2.19 (m, 12H, CH_2), 0.90 (m, 72H, CH_2), 0.49−0.63 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CS_2/CDCl_3$, 75 MHz, ppm): δ 155.6, 154.3, 154.2, 153.7, 153.0, 152.9, 147.2, 146.7, 146.6, 146.24, 146.21, 146.14, 146.08, 146.05, 146.00, 145.95, 145.80, 145.74, 145.65, 145.51, 145.45, 145.35, 145.31, 145.25, 145.20, 145.14, 145.11, 145.03, 145.00, 144.58, 144.52, 144.23, 143.02, 142.87, 142.57, 142.47, 142.16, 142.06, 142.03, 142.00, 141.93, 141.84, 141.55, 141.50, 140.08, 139.88, 139.72, 139.57, 137.78, 137.75, 137.63, 137.03, 136.57, 135.76, 133.1, 132.3, 131.8, 128.9, 124.8, 123.9, 122.9, 122.2, 121.9, 119.1, 118.8, 88.0, 79.4, 76.9, 69.9, 68.6, 55.6, 40.3, 37.0, 31.5, 29.6, 24.0, 22.4, 13.9. MALDI-TOF-MS: *m*/*z* 5311 (M^+).

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Supporting Information Available: Detailed experimental procedures and all characterization data of all new compounds **5**−**44** (PDF, 155 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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