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Synthesis and Optoelectronic Properties of *Janus*-Dendrimer-Type Multivalent Donor−Acceptor Systems

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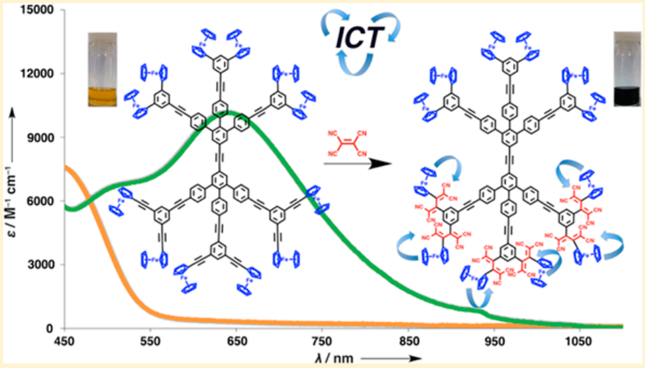
Supporting Information



ABSTRACT: A convergent, multistep protocol was employed for the synthesis of a *Janus*-type multivalent donor−acceptor system. The synthetic approach is based on a Sonogashira cross-coupling of two differently ferrocene-(Fc) substituted dendrons and a final sixfold [2 + 2] cycloaddition−retroelectrocyclization (CA−RE) reaction with tetracyanoethene, which occurs regioselectively at only one of the rigidly linked dendrons. The structural and optoelectronic properties of the compounds were investigated by X-ray analysis, UV/vis spectroscopy, and electrochemistry. The target *Janus*-system displays redox-amphoteric behavior. The nonalkynylated Fc end groups in one dendron are readily and reversibly oxidized. The second dendron, in which the terminal Fc-activated alkynes underwent the CA−RE reaction to give tetracyanobuta-1,3-dienes in the final step of the synthesis, undergoes four reversible 3-e$^-$ reductions in the very narrow potential range of 1 V. A spontaneous intramolecular charge transfer from the donor into the acceptor hemisphere was not observed. Furthermore, the oxidation potential of the Fc donors in one hemisphere is hardly perturbed by the push−pull acceptors in the other, which suggests that electronic communication along the π-system, with several *meta*-connectivities, is not efficient. Therefore, the charge-transfer bands seen in the *Janus*-type system originate from the interaction of the Fc donors with the directly connected tetracyanobuta-1,3-diene acceptors in the same hemisphere.

■ INTRODUCTION

Dendrons and dendrimers are among the most popular multivalent systems.[1] Most known dendrimers feature a single type of end group to ensure synthetic feasibility. Those built from dendrons with different, orthogonal functional end groups, however, are desirable. They allow the formation of polar systems, which have been coined *Janus*-dendrimers, bearing the name of the mythological two-faced god of beginnings and transitions in ancient Roman religion who looks to the future and past.[2] The first *Janus*-dendrimer was reported by Fréchet and co-workers and was obtained by a convergent synthetic strategy using dendrons of different polarities.[2a] The resulting spherical dendrimer was amphiphilic, featuring one side with lipophilic benzyl end groups and the other with polar terminal carboxylates. *Janus*-dendrimers have been investigated for various molecular functions, such as drug delivery, catalysis, and liquid crystalline organization.[2h,k,3] They also enabled self-assembly to a variety of supramolecular systems and shapes.[4]

Dendrimers with redox-active end groups have attracted much attention. Peripheral decoration with electron donor termini yielded systems that underwent multiple reversible oxidation steps in cyclic voltammetry (CV), as reported in particular for ferrocene (Fc) end groups by Astruc and co-workers.[5] The group of Nierengarten described the synthesis of dendrimers with multiple electron-accepting groups, in particular fullerenes, lining the pheriphery, which feature multiple reversible reduction steps in their CV traces.[6] Our group prepared multivalent dendrimer-type systems with up to 12 terminal *N,N*-dialkylanilino-activated buta-1,3-diynes that underwent a [2 + 2] cycloaddition−retroelectrocyclization (CA−RE) reaction with tetracyanoethene (TCNE)[7] to give donor-substituted tetracyanobuta-1,3-diene (TCBD) end groups undergoing both reversible electron oxidation and reduction steps in CV.[8]

While dendritic systems with either multiple donor, multiple acceptor, or push−pull donor−acceptor end groups are well studied, *Janus*-dendrimer-type multivalency systems with strong electron-donor and strong electron-acceptor hemispheres have not been reported. Our goal in this project was to develop an efficient synthesis for such systems. Both

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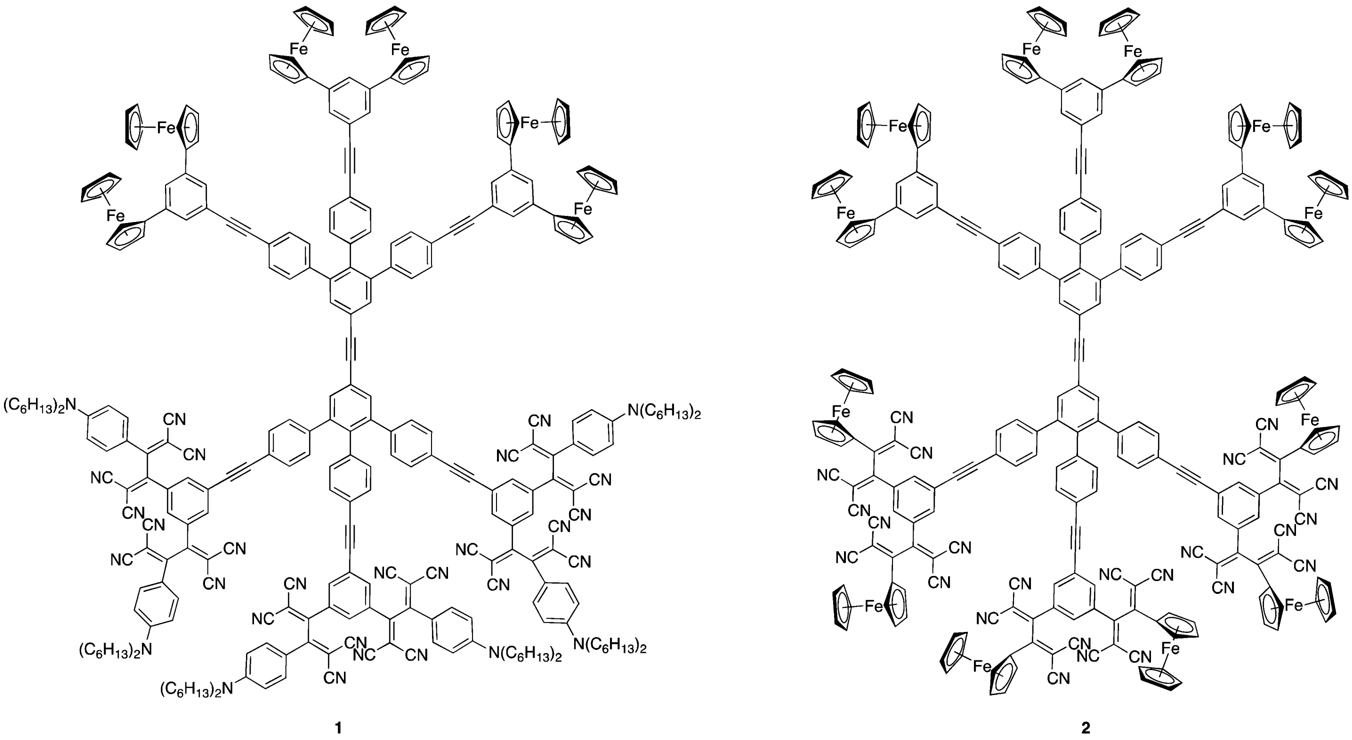
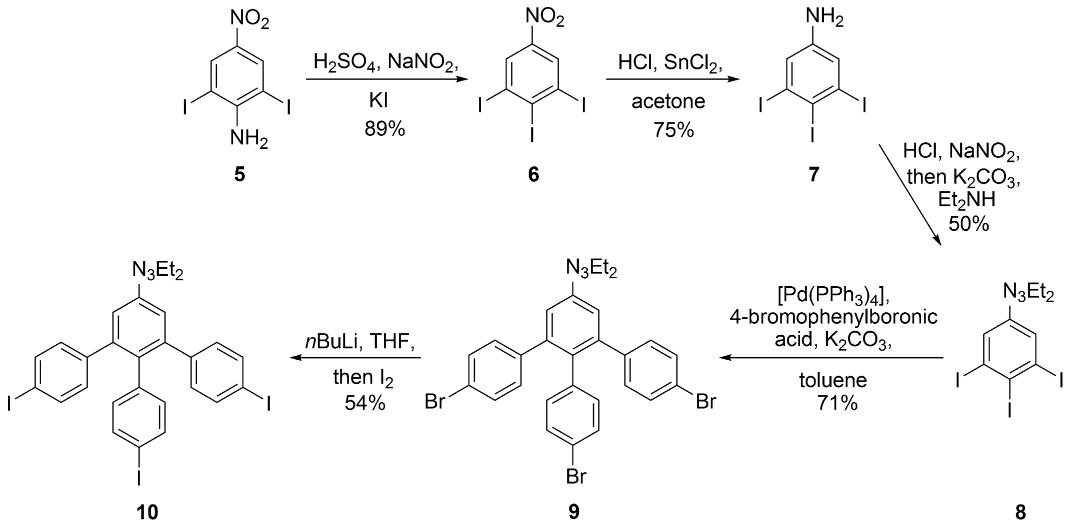


Figure 1. Targeted *Janus*-dendrimer-type multivalency systems **1** and **2** featuring an electron-donor hemisphere and an electron-acceptor hemisphere.

Scheme 1. Synthesis of Precursor 10 to Dendron 3

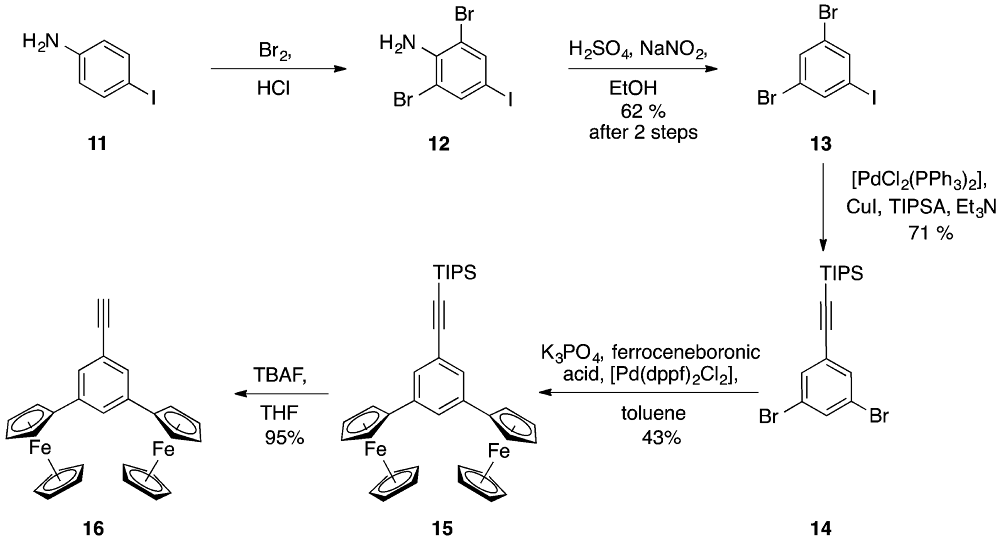


target compounds **1** and **2** possess one hemisphere comprising Fc donor termini, whereas the second hemisphere features different donor-substituted TCBDs, originating from the CA−RE reaction, as strong electron acceptors (Figure 1). We were interested in exploring whether spontaneous intramolecular charge transfer from the donor into the acceptor hemisphere under formation of zwitterionic *Janus*-dendrimer-type system would occur, as had previously been observed in case of a simpler push−pull chromophore.[9] Here, we report the synthesis and optoelectronic properties of **2** and the difficulties that ultimately prevented the preparation of **1**.

■ RESULTS AND DISCUSSION

Synthesis of Dendrons 3 and 4. The core of the target structures is reminiscent of dendrimer cores first introduced by Moore and co-workers.[10] The reaction sequence to access dendron **3**, needed for the construction of both **1** and **2**, starts with the conversion of 2,6-diiodo-4-nitroaniline (**5**)[11] to 1,2,3-triiodo-5-nitrobenzene (**6**)[12] via a Sandmeyer reaction (Scheme 1). Following $SnCl_2$-mediated reduction, 3,4,5-triiodoaniline **7** was obtained in 75% yield.[12] Diethyltriazene **8** was prepared by trapping the diazonium salt from **7** with diethylamine.[13] The NMR spectral data at 298 K showed two different sets of ethyl resonances due to the restricted rotation around the N−N bond.[14] The next step was the threefold *Suzuki* coupling[15] with 4-bromophenylboronic acid to afford

Scheme 2. Synthesis of Precursor 16 to Dendron 3



compound **9**,[16] which was then converted into the more reactive iodo compound **10** by halogen-metal exchange and subsequent quenching of the lithiated intermediate with iodine (Scheme 1). The structures of compounds **9** and **10** were confirmed by X-ray analysis (Scheme 1). Similarly, the synthesis of precursor **16** to dendron **3** started from 4-iodoaniline (**11**), from which compound **14** was prepared via **12** and **13**, according to literature procedures.[17] Suzuki coupling of compound **14** with ferroceneboronic acid afforded compound **15**,[18] and removal of the TIPS group with nBu$_4$NF in wet THF gave dendron precursor **16** (Scheme 2).

Sonogashira coupling[19] of alkyne **16** with triiodide **10** provided triazene **17**, which was converted into aryl iodide **18** upon treatment with MeI (Scheme 3). Sonogashira coupling of **18** with TMS-acetylene afforded **19**, and alkyne-deprotection yielded target dendron **3** (Scheme 3). The ^{1}H and ^{13}C NMR spectra of **3** reflected its C_{2v} symmetry (Figures S36 and S37 in the Supporting Information).

The synthesis of the second dendron **4** for the preparation of target *Janus*-system **1** also started from 2,6-diiodo-4-nitroaniline (**5**) and proceeded via a 9-step protocol (Schemes 4 and 5). Diazonium chemistry was used to transform **5** into 1,3-diiodo-5-nitrobenzene (**20**).[20] SnCl$_2$-mediated reduction gave **21**,[21] which was transformed via the diazonium ion into diethyltriazene **22** (Scheme 4).[13] Sonogashira coupling of **22** with an excess of 4-ethynyl-*N*,*N*-dihexylaniline (**23**)[22] provided **24**. To avoid any quaternization of aniline moieties, Me$_3$SiCl/NaI under relatively mild conditions (CCl$_4$/MeCN, 60 °C, 20 min.) was used instead of MeI to afford iodo compound **25**.[23] Sonogashira coupling of **25** with TMS-acetylene gave **26**, which was deprotected to terminal alkyne **27** (Scheme 4).

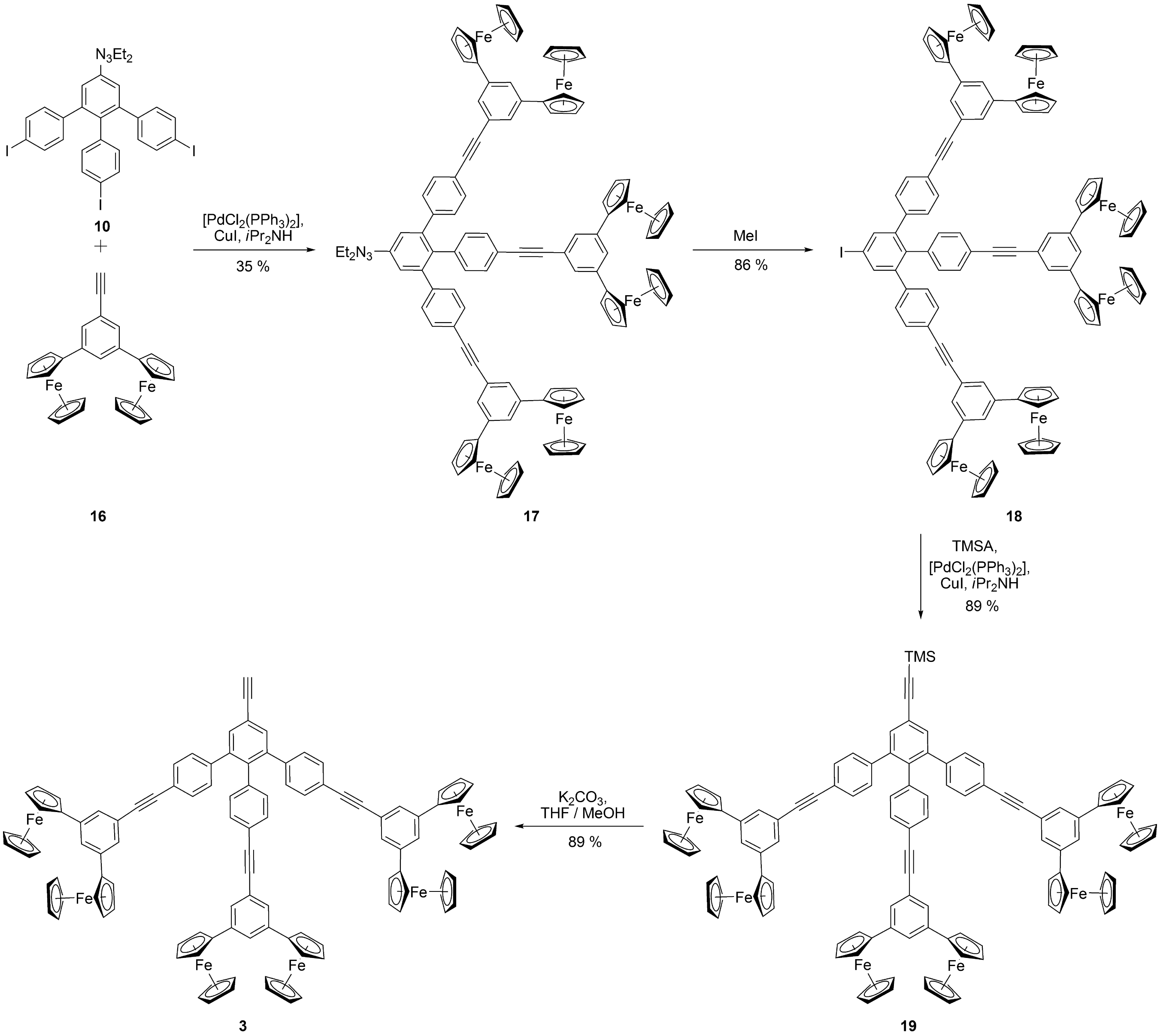
Triazene **28** was obtained by Sonogashira coupling of **27** with **10** (Scheme 5). Unfortunately, multiple attemps (treatment with Me$_3$SiCl/NaI or MeI) to prepare target dendron **4** failed due to problems with the quaternization of the aniline moieties, which could not be avoided. We abandoned the synthesis of **1** due to this roadblock in the final step and turned to the multivalent *Janus*-dendrimer-type system **2** featuring all-Fc donors in both dendrons, thereby eliminating the aforementioned synthetic limitations.

Synthesis of Dendron 29. For the preparation of *Janus*-dendrimer-type system **2**, two dendrons were required for Sonogashira coupling: dendron **3** and the new dendron **29**. The synthesis of **29** started from commercially available 1,3,5-tribromobenzene (**30**), which was subjected to a single Sonogashira coupling with TMS-acetylene to give alkyne **31**. Halogen-metal exchange and subsequent treatment with iodine afforded **32**, which was doubly cross-coupled with ethynylferrocene to yield compound **33**, and by deprotection terminal alkyne **34**. The structure of **33** was confirmed by X-ray analysis (Scheme 6). Sonogashira coupling of alkyne **34** with iodo derivative **10** provided triazene **35**, which was converted to dendron **29** upon treatment with MeI (Scheme 6). The ^{1}H and ^{13}C NMR spectra of **29** confirmed its C_{2v}-symmetric structure (Figures S54 and S55, Supporting Information).

Synthesis of *Janus*-Dendrimer-Type Donor–Acceptor System 2. Sonogashira coupling between dendrons **3** and **29** delivered the multivalent precursor **36** to target **2** in 57% yield (Scheme 7). Its formation, however, was accompanied by homocoupling of terminal alkyne **3** to afford **37** as a byproduct in 20% yield. Compounds **36** and **37** were purified by recycling gel permeation chromatography (R-GPC, column: JAI-gel 2H with CHCl$_3$ as eluent). In order to avoid the unwanted dimerization, a copper-free Sonogashira reaction between dendrons **3** and **29** was also attempted, but no reaction was observed.[24]

The precursor **36** features 12 terminal Fc groups. In one hemisphere, they are attached directly to a phenyl ring, whereas, in the other, they are coupled to acetylenes, which become activated by the electron-donating metallocenes[25] to undergo the CA–RE reaction with TCNE. With compound **36** in hand, we performed the key CA–RE step with TCNE, which gratifyingly afforded the charge-transfer *Janus*-system **2** as a dark green solid (Scheme 7). The structure of **2** was confirmed by HR-MALDI-MS (m/z = 4354.5059, calc. for $C_{266}H_{154}Fe_{12}N_{24}^+$: 4354.5090) (Figure 2). Additionally, we subjected the mixture of the dendritic systems **36** and **37** to the CA–RE reaction with TCNE. When the mixture **36**/**37** was reacted with an excess (12 equiv) of TCNE in (CH$_2$Cl)$_2$, a crude product mixture was isolated that, in the mass spectrum (HR-MALDI-MS), showed two major ions corre-

Scheme 3. Synthesis of Dendron 3

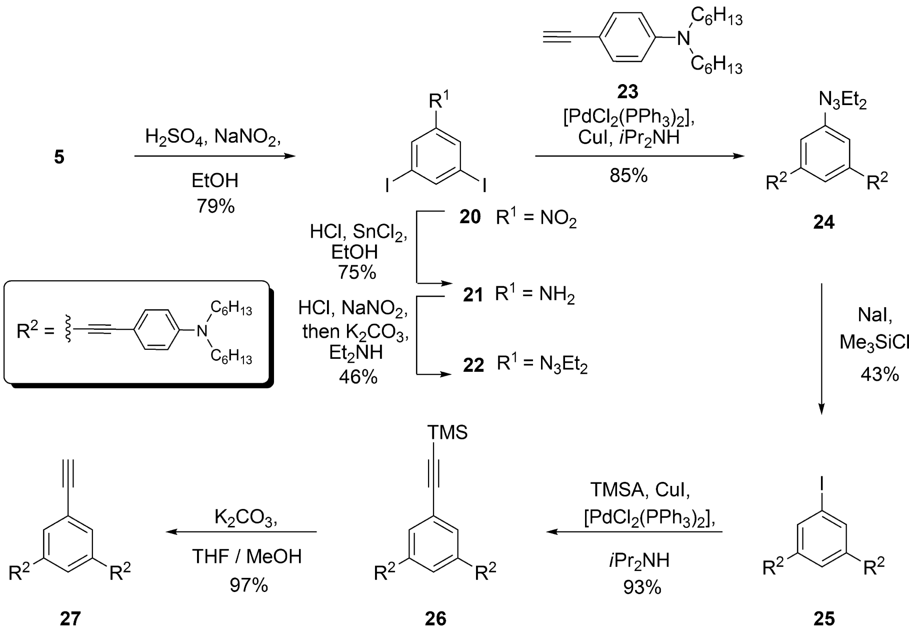


sponding to target compound **2** originating from the addition of 6 TCNE moieties (*m*/*z* = 4354.4866, calc. for $C_{266}H_{154}Fe_{12}N_{24}^+$: 4354.5090) and unreacted **37** (*m*/*z* = 3466.4399, calc. for $C_{220}H_{154}Fe_{12}^+$: 3466.4350) (Figure S17 in the Supporting Information). This approach allowed for the easy separation of **2** from byproduct **37** left from the previous step by R-GPC (column: JAI-gel 2H with $CHCl_3$ as eluent) (Figure S15 in the Supporting Information). Compound **36** was fully converted to **2**, whereas **37** stayed unreacted during the reaction, confirming our hypothesis that only alkynes, which are directly activated by an adjacent donor, will react.

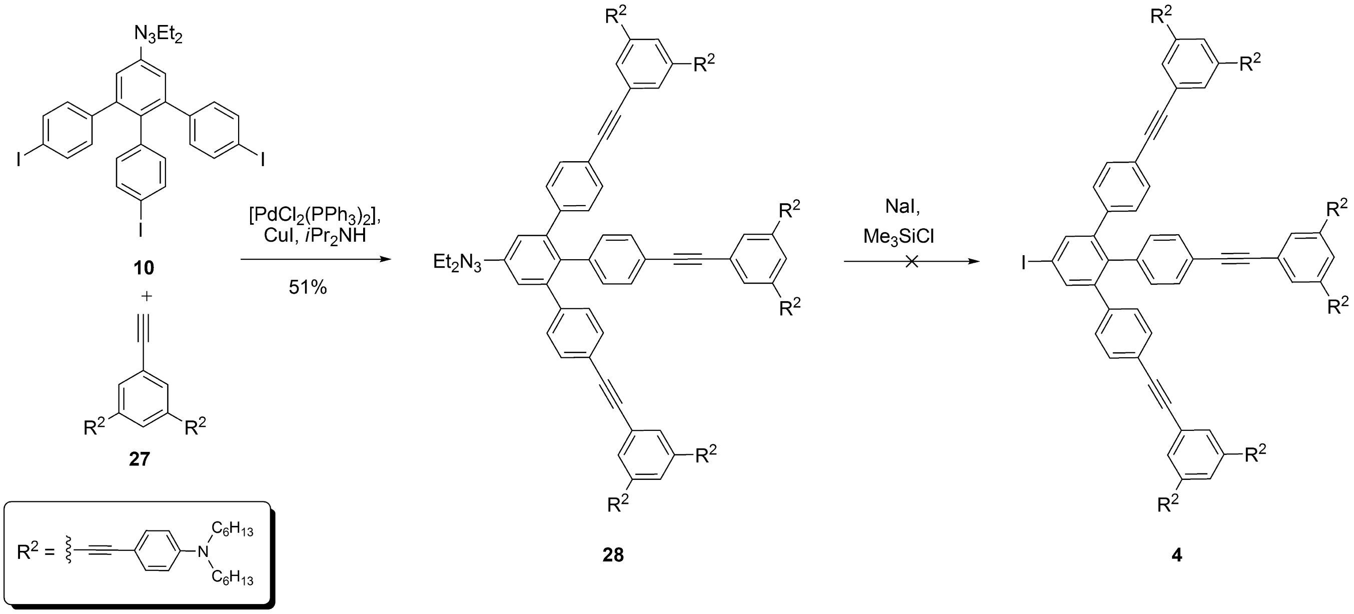
The ^1H and ^{13}C NMR spectra (Figures S64 and S65 in the Supporting Information) measured at room temperature, on the other hand, showed a complex signal pattern, which did not seem in agreement with the proposed C_{2v} symmetry of **2**. This is in contrast to the NMR spectra of **36** and **37**, which reflected the symmetry of the molecules, and therefore, the spectral complexity must be related to the formation of the Fc-substituted TCBD moieties. We had in previous work observed the complication of the interpretation of the ^1H and ^{13}C NMR spectra of both dendrimer-type and acyclic oligomeric push–pull chromophores resulting from the CA–RE reaction, reflecting complex conformational equilibria and the existence of rotamers in solution.[8,26] We decided to run a series of control experiments to confirm this hypothesis.

Investigation of Rotamer Equilibria on Model Systems. We used compounds **38** and **39** (Figure 3) as model systems for the multivalent system **2**. They were prepared by the CA–RE reaction of the acetylenic substrates **27** and **34** with TCNE. Two products were formed according to the ^1H NMR spectrum in the reaction of ferrocene-substituted **34**. In contrast, only one product was obtained in the transformation of the anilino derivative **27**. We subsequently monitored the progress of the reaction of **34** by ^1H NMR spectroscopy in $CDCl_3$ at 298 K (Figures S66 and S67, Supporting Information). Initially, CA and CA–RE reactions take place to form monoadducts. After 4 h, we observed the compound formed by a single CA–RE reaction

Scheme 4. Synthesis of Precursor 27 to Dendron 4



Scheme 5. Attempted Synthesis of Dendron 4

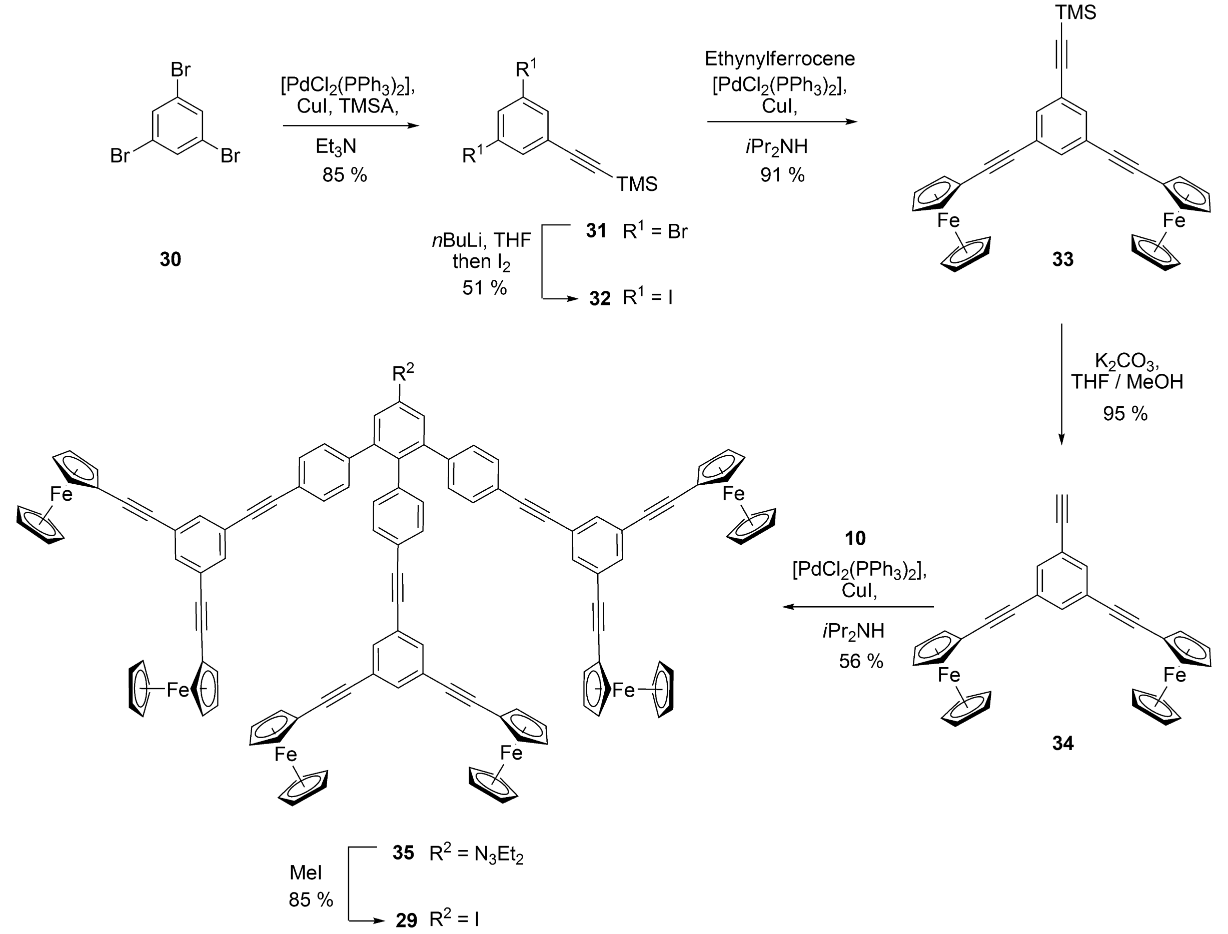


as the predominant product. After 8 h, a second CA–RE reaction with TCNE took place under formation of **39**. We propose that the two products seen in the NMR spectra of **39** are rotamers originating from severe steric crowding in the compound. Calculations at the B3LYP/6-31G** + LANL2DZ level of theory gave a series of minima structures for model compound **39** within 3 kcal mol^{-1} above the global minimum.[27] ^{1}H NMR predictions and structure-chemical shift relations further supported our rotamer proposal (for further details on the computational investigations and methods, see the Supporting Information).

To further investigate and characterize the two species formed in the CA–RE reaction of ferrocene-substituted **39**, we tried to separate and purify them. However, all attempts to separate these species from each other were unsuccessful. Only one spot was detected on the TLC in all tested eluent mixtures (CH_2Cl_2/hexane 99:1 to 1:99, EtOAc/hexane 99:1 to 1:99). Additionally, GPC and HPLC separation attempts on both **2** and **39** only caused peak broadening without any separation (Figure S14, Supporting Information).

Mass spectrometric analysis (HR-MALDI-MS) of the mixture showed only a single peak corresponding to the molecular formula of **39** (m/z = 774.0660, $C_{44}H_{22}Fe_2N_8^+$: 774.0662), suggesting that we had obtained two, presumably conformationally isomeric, species with the same molecular weight (Figure S19, Supporting Information). Additional support for their structures is provided by the ^{1}H NMR spectrum. Both rotamers feature aromatic doublet and triplet signals between 7 and 8 ppm and the terminal acetylene signal around 3 ppm. These patterns can only be obtained if

Scheme 6. Synthesis of Dendron 29



the groups in the push–pull systems in the *meta* position to the terminal acetylene have the same chemical environment.

We measured VT-^{1}H NMR spectra (500 MHz, $(\mathrm{CDCl_2})_2$) from 30 to 120 °C (Figure S68, Supporting Information). No interconversion was detected between the species, and the spectra only featured temperature-dependent shifts of the aromatic protons. Crystals of **39** suitable for X-ray analysis were obtained by slow evaporation from EtOAc/hexane solution at 20 °C (Figure 4).

The structure of compound **39** confirmed the double CA–RE addition of TCNE. According to the crystal packing, only one of the rotamers crystallized (Figure 4; Figures S7 and S8, Supporting Information). Packing effects could be one explanation for the crystallization of only one conformer. Thus, we decided to investigate the mother liquor and the rest of the crystals. The separated mother liquor was colorless, and none of **39** was detected by ^{1}H NMR spectroscopy following evaporation of the solvent. Powder XRD is the most appropriate method to compare the identity of the remaining crystal bulk. Unfortunately, this could not be utilized due to the ethyl acetate present in the crystal packing and the large cell volume. Therefore, 15 random crystals were measured, and the results for all of them were in good agreement with the first X-ray analysis (Figure 4). A mixture of two conformers was again observed by ^{1}H NMR spectroscopy after dissolving the X-ray-measured crystals.

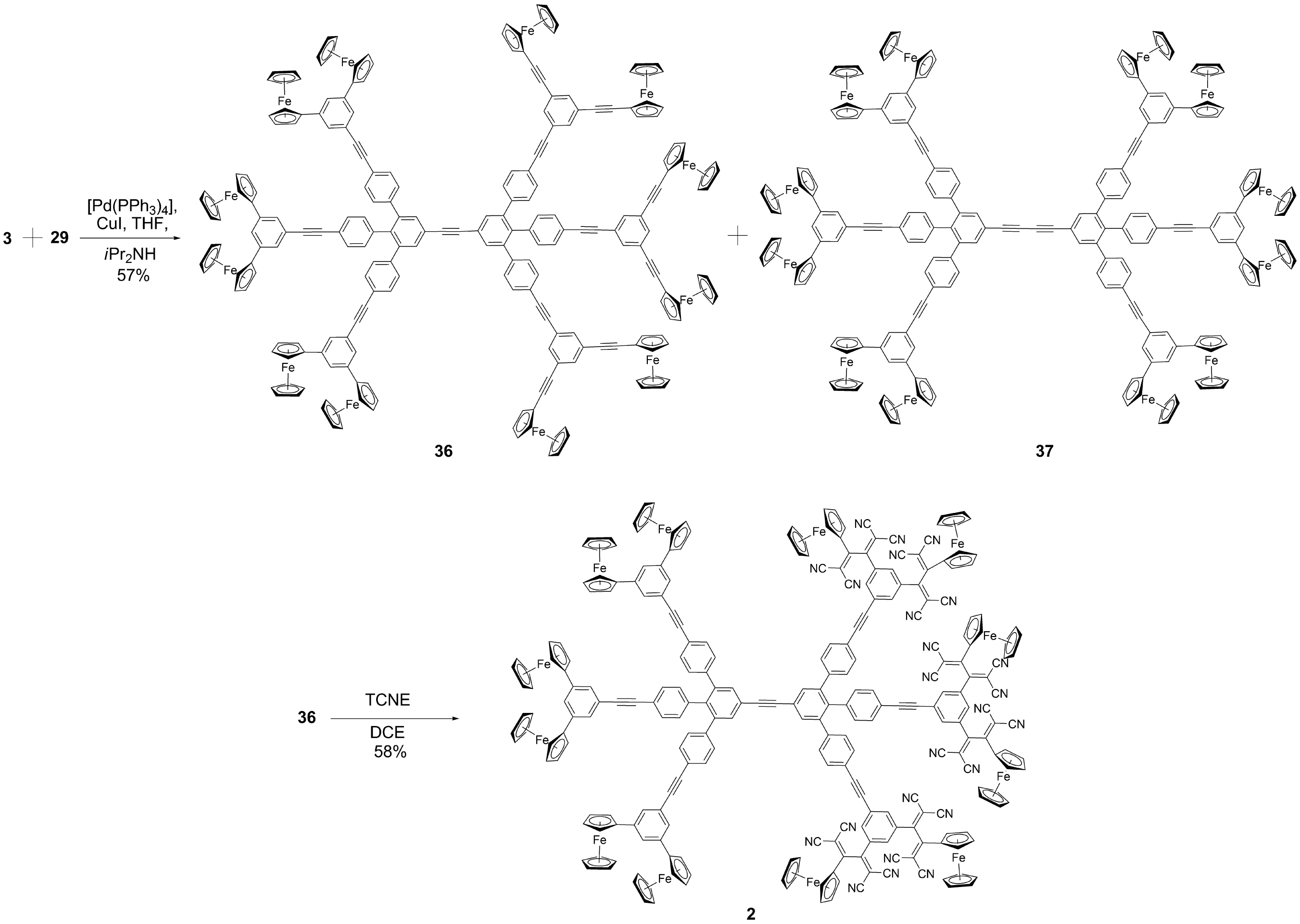
Taken together, these experiments suggest that two highly stable rotamers are formed in near equal amounts in the double CA–RE reaction of **34** with TCNE to give bis-TCBD derivative **39**. It is clear that the spectral situation must be severely complicated in the case of **2**, which is formed by six CA–RE reactions in proximity to ferrocenes, and therefore, the control studies support our hypothesis that the NMR spectra of **2** are complicated by the presence of a complex mixture of noninterchanging rotamers.

UV/vis Spectroscopy. During the reaction of compound **36** with TCNE, the color of solutions in $(\mathrm{CH_2Cl})_2$ changed from orange to dark green. In agreement with this visible observation, a broad intramolecular charge-transfer (CT) band appears at $\lambda_{\mathrm{max}} = 643$ nm (1.93 eV, $\varepsilon = 10\,100$ M^{-1} cm^{-1}) with the end absorption reaching into the near-infrared region (Figure 5).[28] The spectra of compounds **36** and **37** without push–pull TCBD moieties lack this intense bathochromically shifted band (Figure 5).

A key question is the origin of this CT band: does it arise from intramolecular CT between the stronger (see electrochemical data below) Fc donors in one hemisphere to the TCBD acceptors in the second, or is the CT mainly a feature of the (weaker) Fc donors interacting with the directly attached TCBD moieties? In other words, is there electronic communication between the two hemispheres in *Janus*-system **2**? Unfortunately, size and conformational flexibility of **2** prevented us to address this question by precise computational study.

Experimentally, the absence of long-distance CT interactions through the *Janus*-system was confirmed by comparing

Scheme 7. Synthesis of *Janus*-Dendrimer-Type Donor–Acceptor System 2



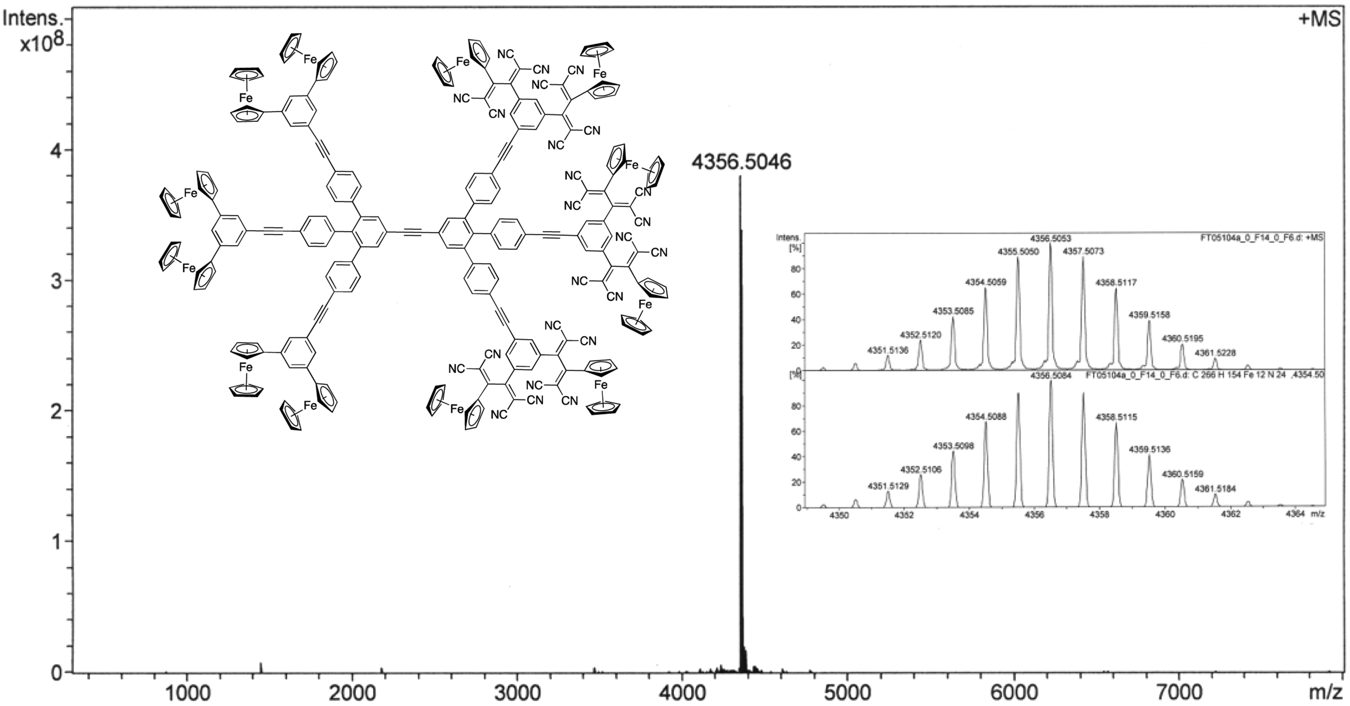


Figure 2. HR-MALDI-MS spectrum (DCTB as matrix) of *Janus*-dendrimer-type donor–acceptor system **2**.

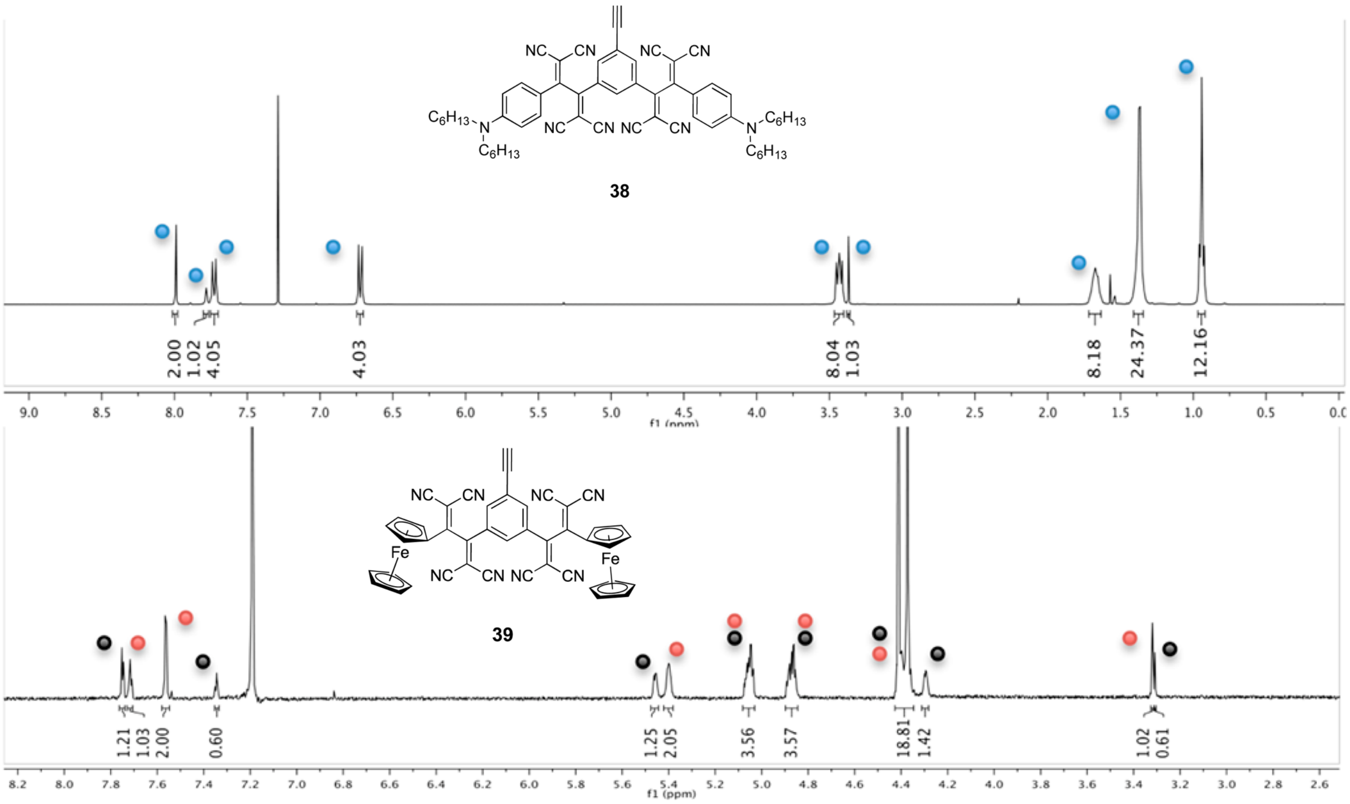


Figure 3. ^{1}H NMR spectra (400 MHz) of compounds **38** and **39** in $CDCl_3$ at 298 K. Set of peaks for the products are highlighted with “blue”, “red”, and “black” circles.

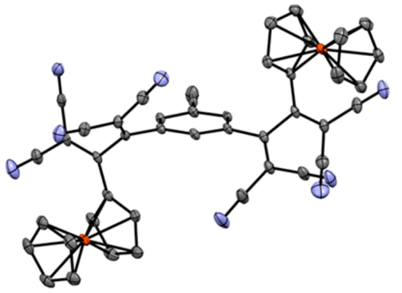


Figure 4. ORTEP representation of **39** with vibrational ellipsoids shown at the 50% probability level, T = 100 K. H atoms and solvent molecules are omitted for clarity.

the UV/vis spectra of **2** and model system **39**. Compound **39** shows an intramolecular CT band at λ_{max} = 640 nm (1.94 eV, ε = 2500 M^{-1} cm^{-1}) (Figure 6). Not only the maxima but also the overall shapes of the CT bands in both **2** and **39** are quite similar. The higher molar extinction coefficient of the CT band in the spectrum of **2** can be readily explained by the fact that the *Janus*-system contains three substructures corresponding to **39**.

On the basis of these experimental findings, we suggest that there is no electronic communication between the two hemispheres in *Janus*-dendrimer-type system **2** and that charge-transfer transitions are due to the independent Fc-substituted TCBD push−pull chromophores in one hemisphere. The long π-bridge with two or more *meta*-connectivities between the Fc donors in one hemisphere and the TCBD acceptors in the other prevents their electronic communication.

Electrochemistry. Cyclic voltammetry (CV; Table 1; Figures S10−S12, Supporting Information) and rotating disk voltammetry (RDV; Table 1) in CH_2Cl_2 (+ 0.1 M nBu$_4$NPF$_6$, internal standard Fc$^+$/Fc) revealed that model compounds **38** and **39** undergo one reversible oxidation whose peak characteristics are those of a one-electron transfer. However, the wave amplitudes observed by RDV indicate that this oxidation step involves two electrons. The appearance of a two-electron process indicates that both ferrocene and DAA (dialkylanilino) donor groups behave as independent redox centers.[7b] Both compounds exhibit four TCBD-centered reduction steps with well-resolved one-electron transfers.

The dendrimer-type systems **36** and **37** show only one oxidation step on the available potential range. The anodic peak of **37** has the characteristics of a reversible one-electron transfer from the shape of the peak. Oxidation of the ferrocenes occurs at the same potential, denoting that they behave as independent redox centers. An observed redissolution peak implies that the 12-electron-oxidized species precipitate on the electrode surface and undergo a reduction to the soluble neutral species on the reverse scan. This behavior may result from the poor solubility of highly charged species in CH_2Cl_2. A similar behavior is observed for **36**, but the two sets of ferrocenes are oxidized at different potentials, as shown by the presence of a shoulder on the oxidation peak. Nevertheless, the oxidized species are insoluble and similar to **37**; a redissolution peak is observed on the reverse scan.

The target *Janus*-system **2** gave rise by CV to two oxidation steps, the first one being reversible, whereas the second oxidation shows characteristics of a deposit formation on the electrode surface during oxidation, followed by a redissolution peak on reduction. The first reversible oxidation occurs on the

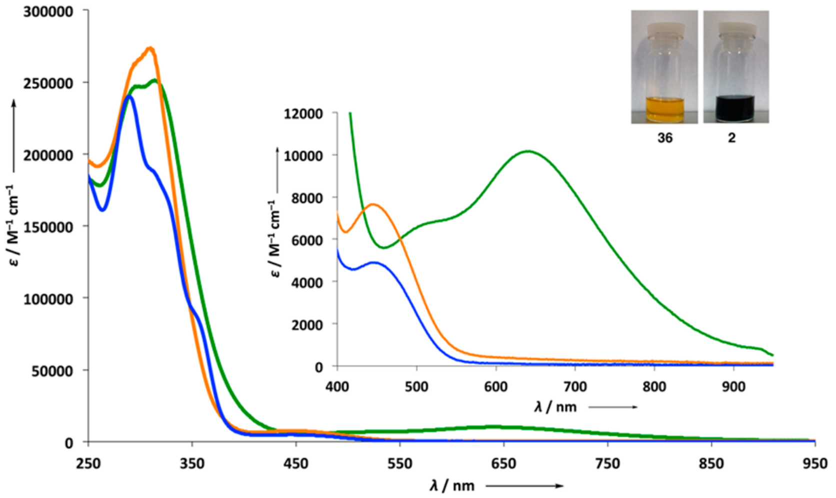


Figure 5. UV/vis spectra of compounds **2** (green line), **36** (orange line), and **37** (blue line) in CH_2Cl_2 at 298 K.

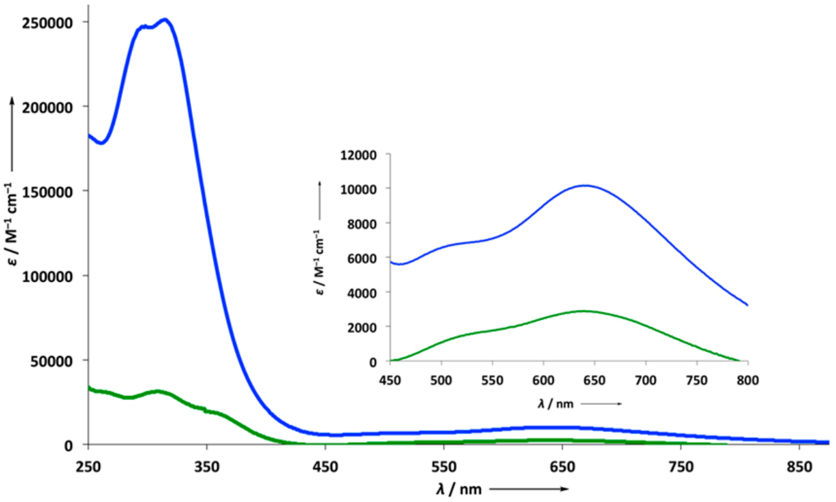


Figure 6. UV/vis spectra of compounds **2** (blue line) and **39** (green line) in CH_2Cl_2 at 298 K.

six aryl-bound Fc moieties at the typical potential of E° = +0.00 V. On the other hand, the irreversible oxidation of the six TCBD-conjugated Fc moieties at E_p = +0.43 V is strongly anodically shifted.[25b]

The reduction of **2** occurs in four well-separated steps centered on the strongly electron-accepting TCBD moieties at similar potentials to those observed for the model system **39**. The amplitude of limiting current for the first oxidation is twice the amplitude of each of the four reductions. It turns out that each reduction corresponds to an exchange of three electrons.

The fact that the isolated ferrocenes in the one hemisphere are undisturbed in their oxidation potential corroborates the findings from the UV/vis study, that there is no electronic communication with the remote TCBD acceptors. The nice reversibility of this first oxidation is an indication that the generated hexacation remains perfectly soluble in our experimental conditions. According to the spectroelectrochemical investigations, no spectral changes are observed during the first oxidation process. However, small changes were observed during reduction, as shown in Figure S13 (Supporting Information). Observed spectral evolutions are quite similar at the plateau potential of the second and fourth reduction steps.

■ CONCLUSION

An efficient multistep synthesis of the ferrocene-containing *Janus*-dendrimer-type donor−acceptor system **2** was reported. Two dendrons, one with Fc moieties directly attached to benzene rings and one with Fc moieties attached to acetylenes, are connected by Sonogashira cross-coupling. The Fc-moieties activate the adjacent acetylenes, and TCNE undergoes an efficient [2 + 2] cycloaddition−retroelectrocyclization under formation of push−pull donor-substituted tetracyanobuta-1,3-dienes (TCBDs). This synthetic route should also enable the introduction of even more potent electron acceptors, such as TCNQ and F_4-TCNQ, which also undergo the CA−RE reaction.[9] We performed a series of test experiments to explain the observation of rotamers in the NMR spectra of **2**. The UV/vis spectrum of this *Janus*-system clearly shows the formation of a broad intramolecular CT band, with the end absorption reaching into the near-infrared region. UV/vis spectral comparisons reveal that there is no communication between the hemispheres of the target dendritic system and that the independent push−pull chromophoric units in one hemisphere are responsible for the CT transitions. Electrochemical study confirms that the ferrocenes in the two hemispheres of **2** behave as independent

Table 1. Electrochemical Data Measured by Cyclic Voltammetry (CV) and Rotating Disk Voltammetry (RDV) in CH_2Cl_2 + 0.1 M $n$$Bu_4NPF_6$[a,h]

	CV			RDV	
	$E°$ [V][b]	ΔE_p [mV][c]	E_p [V][d]	$E_{1/2}$ [V][e]	slope [mV][f]
2			+0.43		
	+0.00	60		+0.00 (6e$^-$)	60
	−0.67	100		spread out unresolved waves	
	−0.95	120			
	−1.27	95			
	−1.37	75			
36			+0.19[g]	+0.17 (6e$^-$)	
			+0.08[g]	+0.05 (6e$^-$)	70
37			+0.08[g]	+0.05 (12e$^-$)	55
38	+0.89	100		+0.91 (2e$^-$)	60
	−0.77	110		−0.82 (1e$^-$)	60
	−0.97	110		−1.04 (1e$^-$)	60
	−1.25	90		−1.30 (1e$^-$)	80
	−1.38	130		−1.50 (1e$^-$)	100
39	+0.48	80		+0.49 (2e$^-$)	60
	−0.72	100		−0.74 (1e$^-$)	60
	−0.90	100		−0.95 (1e$^-$)	60
	−1.23	100		−1.30 (1e$^-$)	80
	−1.33	100		−1.41 (1e$^-$)	100

[a] All potentials are given versus the Fc^+/Fc couple used as internal standard. Working electrode: glassy carbon electrode; pseudo counter electrode: Pt; reference electrode: Pt. Scan rate: 0.1 V s^{-1}. [b] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{ox} - E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [d] E_p = Irreversible peak potential. [e] $E_{1/2}$ = Half-wave potential. [f] Slope of the linearized plot of E versus $\log[I/(I_{lim} - I)]$, where I_{lim} is the limiting current and I the current. [g] On the reverse scan, a redissolution peak was observed at +0.05 V. [h] All potentials are given versus ferrocene, used as internal standard.

redox centers. The oxidation potentials of the aryl-bound ferrocenes are undisturbed and appear at the typical potential of ferrocenes ($E°$ = 0.00 V), whereas the TCBD-bound Fc moieties feature a strong anodic shift (E_p = +0.43 V). The strong Fc electron donors in one hemisphere are not in electronic communication with the strong electron acceptors in the second: the extended π-system with several *meta*-connectivities behaves similar to a σ-bonded tunneling bridge. Therefore, the described *Janus*-dendrimer-type donor−acceptor system could serve as a new structural motif for molecular rectifiers according to the concept by Aviram and Ratner.[29]

■ EXPERIMENTAL SECTION

General. Reagents were purchased as reagent grade and used without further purification. Solvents for extraction or column chromatography were distilled from technical grade. Dry solvents (THF, CH_2Cl_2, diethyl ether, MeCN, and toluene) for reactions were purified by a solvent drying system under a nitrogen atmosphere (H_2O content < 10 ppm as determined by Karl Fischer titration). All other solvents were purchased in p.a. quality. Reactions in the absence of air and moisture were performed in oven-dried glassware under an Ar or N_2 atmosphere. Flash column chromatography (FC) was performed using SiO_2 (60 Å, 230−400 mesh, particle size 0.040−0.063 mm) at 25 °C with a head pressure of 0.0−0.5 bar. The used solvent compositions are reported individually in parentheses. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F254. Visualization was achieved using UV light (254 or 366 nm) or by staining with iodine adsorbed on SiO_2 or with ceric ammonium molybdate solution (120 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 5 g $(NH_4)_2Ce(NO_3)_6$ in 800 mL 10% H_2SO_4). Evaporation *in vacuo* was performed at 25−60 °C and 900−10 mbar. Reported yields refer to spectroscopically and chromatographically pure compounds that were dried under high vacuum (0.1−0.05 mbar) before analytical characterization. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 600 or 400 MHz (^1H) and 150 or 100 MHz (^{13}C), respectively. Temperatures of measurements are indicated in the procedures and on the spectra. Chemical shifts δ are reported in ppm downfield from tetramethylsilane using the residual solvent signals as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm; CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 53.8 ppm; $(CD_3)_2CO$: δ_H = 2.05 ppm, δ_C = 206.3 ppm). For ^1H NMR, coupling constants J are given in Hz and the resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet), and br. (broad). Infrared (IR) spectra are reported as wavenumbers $\tilde{\nu}$ (cm^{-1}) with band intensities indicated as s (strong), m (medium), w (weak), br (broad). For FT-ICR-MALDI measurements, the matrix was 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) or 3-hydroxypyridine-2-carboxylic acid (3-HPA). The most important peaks are reported in m/z units with M^+ as the molecular ion and with the corresponding intensities in %. UV/vis spectroscopy was recorded on a UV/vis/NIR spectrophotometer. Electrochemical measurements were carried out in CH_2Cl_2 containing 0.1 M $n$$Bu_4NPF_6$ in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). The working electrode was a glassy C disk (3 mm in diameter), the auxiliary electrode was a Pt wire, and the pseudo reference electrode was a Pt wire. The cell was connected to a potentiostat driven by software running on a personal computer. All potentials are given versus Fc^+/Fc used as internal reference and are uncorrected from Ohmic drop. Compounds **6**,[12] **7**,[12] **12**,[17a] **13**,[17a] **14**,[17b] **20**,[20] **21**,[21] **22**,[8] **23**,[22] **31**,[30] and **32**[31] were prepared according to literature procedures.

1-(3,4,5-Triiodophenyl)-3,3-diethyltriaz-1-ene (8). A solution of 3,4,5-triiodoaniline (**7**) (4.14 g, 8.79 mmol) in a mixture of Et_2O/THF/MeCN 7:6:1 (100 mL), was treated with conc. HCl (11 mL), cooled to −5 °C, treated with a solution $NaNO_2$ (2.06 g, 29.89 mmol) in MeCN/H_2O 2:3 (25 mL), and stirred for 1.5 h at −5 °C. The mixture was poured into a cold solution of K_2CO_3 (6.06 g, 43.85 mmol) and diethylamine (3.57 g, 5.03 mL, 48.81 mmol) in MeCN/H_2O 2:1 (150 mL). The mixture was stirred for 3 h at 25 °C and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. FC (SiO_2; hexane/CH_2Cl_2 2:1) gave triazene **8** (2.44 g, 50%) as a brown oil. R_f = 0.57 (hexane/CH_2Cl_2 2:1); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.19 and 1.31 (2 br. s, 6 H), 3.70−3.80 (m, 4 H), 7.90 ppm (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.2, 14.6, 41.6, 49.5, 106.5, 114.4, 131.2, 152.6 ppm; IR (ATR): $\tilde{\nu}$ = 2971 (w), 2930 (w), 1552 (m), 1514 (m), 1448 (s), 1397 (m), 1378 (m), 1330 (s), 1230 (m), 1184 (w), 1107 (m), 1075 (m), 993 (m), 872 cm^{-1} (m); HR-EI-MS (70 eV): m/z (%): 555.8157 (14, $[M + H]^+$, calc. for $C_{10}H_{13}I_3N_3^+$: 555.8165); 454.7278 (45, $[M - C_4H_{10}N_3^+]$, calc. for $C_6H_2I_3^+$: 454.7291).

3,3-Diethyl-1-[3,4,5-tris(4-bromophenyl)phenyl]triaz-1-ene (9). A suspension of **8** (500 mg, 0.9 mmol), 4-bromophenylboronic acid (1.08 g, 5.41 mmol), K_2CO_3 (3.73 g, 27.04 mmol), and Aliquat 336 (11 mg, 0.03 mmol) in toluene (50 mL) was deoxygenated three times via a "freeze−pump−thaw" cycle. $[Pd(PPh_3)_4]$ (121 mg, 0.1 mmol) was added, and the solution was stirred for 18 h at 80 °C. The mixture was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. FC (Al_2O_3; hexane/CH_2Cl_2 4:1) gave **9** (411 mg, 71%) as a yellow greasy solid. R_f = 0.21 (SiO_2; hexane/CH_2Cl_2 4:1); mp 167−168 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.27 (br. t, J = 7.2 Hz, 6 H), 3.79 (br. q, J = 7.2 Hz, 4 H), 6.67 (br. d, J = 8.4 Hz, 2 H), 6.95 (br. d, J = 8.5 Hz, 4 H), 7.15 (br. d, *J* = 8.4 Hz, 2 H), 7.30 (br. d, *J* = 8.5 Hz, 4 H), 7.44 ppm (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 27.1, 120.5, 120.8, 121.9, 130.9, 131.0, 131.6, 133.4, 134.2, 138.2, 140.8, 141,5, 150.6 ppm (13 out of 14 signals expected); IR (ATR): $\tilde{\nu}$ = 2972 (w), 2902 (w), 1590 (m), 1486 (m), 1436 (m), 1395 (m), 1332 (s), 1244 (m), 1071 (m), 1009 (s), 741 (s), 663 (m), 636 cm^{-1} (m); HR-MALDI-MS (DCTB): *m*/*z* (%): 639.9596 (33, [*M* + H$^+$], calc. for $C_{28}H_{25}Br_3N_3^+$: 639.9593), 640.9434 (18), 641.9576 (100), 642.9610 (29), 643.9556 (96), 644.9588 (30), 645.9536 (32).

3,3-Diethyl-1-[3,4,5-tris(4-iodophenyl)phenyl]-triaz-1-ene (10). A solution of 1.6 M *n*BuLi in hexane (4.1 mL, 6.56 mmol) was added dropwise to a solution of **9** (1.00 g, 1.56 mmol) in THF (200 mL) at −78 °C. The mixture was stirred for 20 min at this temperature, treated dropwise with a solution of I_2 (4.73 g, 18.64 mmol) in THF (40 mL), stirred for 30 min, then warmed to 20 °C, diluted with Et_2O, and washed with an aq. 5% $Na_2S_2O_3$ solution and brine. The aqueous phase was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. FC (SiO_2; hexane/CH_2Cl_2 4:1) and crystallization from CH_2Cl_2 gave **10** (657 mg, 54%) as a white solid. R_f = 0.20 (SiO_2; hexane/CH_2Cl_2 4:1); mp 195−196 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.27 (br. t, *J* = 7.2 Hz, 6 H), 3.78 (br. q, *J* = 7.2 Hz, 4 H), 6.54 (d, *J* = 8.3 Hz, 2 H), 6.82 (d, *J* = 8.4 Hz, 4 H), 7.34 (d, *J* = 8.3 Hz, 2 H), 7.42 (s, 2 H), 7.50 ppm (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 92.2, 92.4, 121.9, 131.9, 133.7, 134.1, 136.8, 137.0, 138.8, 141.46, 141.49, 150.7 ppm (12 out of 14 signals expected); IR (ATR): $\tilde{\nu}$ = 2975 (w), 2932 (w), 1586 (m), 1483 (m), 1432 (s), 1398 (m), 1379 (m), 1329 (s), 1221 (m), 1161 (w), 1099 (m), 1076 (m), 1003 (s), 891 (w), 829 (m), 817 (s), 772 (w), 728 cm^{-1} (w); HR-MALDI-MS (DCTB): *m*/*z* (%): 783.9181 (100, [*M* + H$^+$], calc. for $C_{28}H_{25}I_3N_3^+$: 783.9177), 784.9215 (31), 785.9248 (5).

[2-(3,5-Diferrocenylphenyl)ethynyl]triisopropylsilane (15). A solution of **14** (700 mg, 1.68 mmol) and ferroceneboronic acid (850 mg, 3.7 mmol) in toluene (50 mL) was deoxygenated thoroughly by bubbling Ar through for 30 min. K_3PO_4 (1.78 g, 8.39 mmol) and [$PdCl_2(dppf)_2$] (25 mg, 0.031 mmol) were added. The mixture was stirred under Ar at 80 °C for 12 h and evaporated. FC (SiO_2; hexane/CH_2Cl_2 3:1) gave **15** (452 mg, 43%) as an orange foam. R_f = 0.54 (SiO_2; hexane/CH_2Cl_2 3:1); mp 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.18 (s, 21 H), 4.09 (s, 10 H), 4.34 (t, *J* = 1.9 Hz, 4 H), 4.68 (t, *J* = 1.9 Hz, 4 H), 7.38 (d, *J* = 1.7 Hz, 2 H), 7.56 ppm (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.6, 18.9, 66.8, 69.2, 69.8, 84.8, 90.2, 107.7, 123.6, 124.3, 127.4, 139.6 ppm; IR (ATR): $\tilde{\nu}$ = 3093 (m), 2918 (m), 2854 (m), 2212 (s), 1581 (s), 1539 (s), 1463 (w), 1410 (m), 1109 (m), 815 (s), 675 cm^{-1} (w); HR-MALDI-MS (DCTB): *m*/*z* (%): 624.1795 (13), 625.1832 (5), 626.1748 (100, *M*$^+$, calc. for $C_{37}H_{42}Fe_2Si^+$: 626.1749), 627.1785 (37), 628.1823 (7).

1,3-(Diferrocenyl)-5-ethynylbenzene (16). A solution of **15** (500 mg, 0.8 mmol) in THF (25 mL) was treated with a 1 M solution of nBu_4NF in THF (0.94 mL, 0.94 mmol), stirred at room temperature for 2 h, and evaporated. FC (SiO_2; hexane/CH_2Cl_2 1:1) gave **16** (356 mg, 95%) as a red foam. R_f = 0.65 (SiO_2; hexane/CH_2Cl_2 1:1); mp 190−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.12 (s, 1 H), 4.08 (s, 10 H), 4.36 (t, *J* = 1.9 Hz, 4 H), 4.68 (t, *J* = 1.9 Hz, 4 H), 7.44 (d, *J* = 1.7 Hz, 2 H), 7.56 ppm (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 66.7, 69.3, 69.8, 76.8, 84.2, 84.4, 122.1, 124.4, 127.3, 139.9 ppm; IR (ATR): $\tilde{\nu}$ = 3089 (m), 2929 (m), 2203 (w), 1593 (s), 1407 (m), 1253 (m), 1102 (s), 1034 (m), 999 (s), 814 cm^{-1} (s); HR-MALDI-MS (DCTB): *m*/*z* (%): 468.0461 (12), 469.0493 (4), 470.0414 (100, *M*$^+$, calc. for $C_{28}H_{22}Fe_2^+$: 470.0415), 471.0447 (29), 472.0481 (4).

3,3-Diethyl-1-[3,4,5-tris(4-{2-[3,5-di(ferrocenyl)phenyl]-ethynyl}phenyl)phenyl]-triaz-1-ene (17). A solution of **10** (45 mg, 0.06 mmol) in iPr_2NH (10 mL) was deoxygenated thoroughly by bubbling Ar thorough for 30 min, treated with **16** (162 mg, 0.35 mmol), CuI (2 mg, 0.011 mmol), and [$PdCl_2(PPh_3)_2$] (5 mg, 0.007 mmol), and stirred at 40 °C for 14 h. Evaporation, FC (SiO_2; hexane/CH_2Cl_2 1:1) and recycling GPC (JAI 2H; $CHCl_3$) gave **17** (37 mg, 35%) as an orange viscous film. R_f = 0.32 (SiO_2; hexane/CH_2Cl_2 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.32 (br. t, *J* = 7.0 Hz, 6 H), 3.84 (br. q, *J* = 7.0 Hz, 4 H), 4.06 (s, 10 H), 4.09 (s, 20 H), 4.32 (t, *J* = 1.9 Hz, 4 H), 4.35 (t, *J* = 1.9 Hz, 8 H), 4.68 (t, *J* = 1.9 Hz, 4 H), 4.71 (t, *J* = 1.9 Hz, 8 H), 6.91 (br. d, *J* = 8.2 Hz, 2 H), 7.19 (br. d, *J* = 8.3 Hz, 4 H), 7.31 (br. d, *J* = 8.2 Hz, 2 H), 7.43−7.56 (m, 13 H), 7.58 ppm (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 66.6, 66.7, 69.25, 69.27, 69.82, 69.84, 84.5, 84.6, 89.1, 89.2, 90.1, 90.2, 120.8, 121.3, 121.9, 123.28, 123.31, 123.7, 123.8, 126.76, 126.80, 130.2, 131.0, 131.2, 132.1, 135.1, 139.7, 139.8, 139.9, 142.1, 142.2, 150.7 ppm (32 out of 34 signals expected); IR (ATR): $\tilde{\nu}$ = 2970 (w), 2930 (w), 2161 (w), 1587 (s), 1509 (m), 1435 (m), 1408 (m), 1332 (m), 1244 (m), 1105 (s), 1031 (m), 1000 cm^{-1} (s); HR-MALDI-MS (DCTB): *m*/*z* (%): 1805.3078 (4), 1806.3107 (5), 1807.3034 (29), 1808.3059 (36), 1809.2997 (85, *M*$^+$, calc. for $C_{112}H_{87}Fe_6N_3^+$: 1809.2998), 1810.3016 (100), 1811.3042 (66), 1812.3070 (29), 1813.3096 (10), 1814.3115 (3).

1,2,3-Tris{4-[2-(3,5-diferrocenylphenyl)ethynyl]phenyl}-5-iodobenzene (18). A solution of **17** (100 mg, 0.06 mmol) in MeI (5 mL) was deoxygenated thoroughly by bubbling Ar for 30 min and then stirred in a sealed tube at 120 °C for 16 h. Evaporation and FC (Al_2O_3; hexane/CH_2Cl_2 3:1) gave **18** (87 mg, 86%) as a red viscous foam. R_f = 0.11 (SiO_2; hexane/CH_2Cl_2 3:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.05 (s, 10 H), 4.08 (s, 20 H), 4.32 (t, *J* = 1.9 Hz, 4 H), 4.35 (t, *J* = 1.9 Hz, 8 H), 4.67 (t, *J* = 1.9 Hz, 4 H), 4.70 (t, *J* = 1.9 Hz, 8 H), 6.86 (br. d, *J* = 8.3 Hz, 2 H), 7.11 (br. d, *J* = 8.3 Hz, 4 H), 7.31, (br. d, *J* = 8.3 Hz, 2 H), 7.40−7.60 (m, 13 H), 7.86 ppm (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 66.66, 66.69, 69.29, 69.30, 69.8, 69.9, 84.47, 84.52, 88.8, 88.9, 90.5, 90.7, 93.5, 121.6, 122.0, 123.1, 123.2, 123.9, 124.0, 126.76, 126.80, 130.0, 131.2, 131.4, 131.6, 138.2, 138.4, 138.6, 139.79, 139.83, 140.2, 143.4 ppm; IR (ATR): $\tilde{\nu}$ = 2953 (w), 2868 (w), 2234 (w), 1587 (s), 1507 (m), 1437 (m), 1410 (m), 1385 (m), 1251 (m), 1106 (s), 1032 (m), 999 cm^{-1} (s); HR-MALDI-MS (DCTB): *m*/*z* (%): 1833.1277 (6), 1834.1205 (29), 1835.1237 (36), 1836.1172 (83, *M*$^+$, calc. for $C_{108}H_{77}Fe_6I^+$: 1836.1167), 1837.1188 (100), 1838.1215 (64), 1839.1245 (29), 1840.1273 (9), 1841.1300 (3).

(2-{3,4,5-Tris(4-[2-(3,5-diferrocenylphenyl)ethynyl]phenyl}-ethynyl)trimethylsilane (19). Ethynyltrimethylsilane (18 μL, 0.13 mmol), [$Pd(PPh_3)_2Cl_2$] (13 mg, 0.019 mmol), and CuI (5 mg, 0.026 mmol) were added to a deoxygenated solution of **18** (110 mg, 0.06 mmol) in (iPr)$_2$NH (25 mL) under a nitrogen atmosphere. The mixture was stirred at 25 °C for 14 h and filtered through a silica plug. Evaporation and FC (SiO_2; hexane/CH_2Cl_2 2:1) gave **19** (96 mg, 89%) as a red solid. R_f = 0.12 (SiO_2; hexane/CH_2Cl_2 2:1); mp > 240 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.31 (s, 9 H), 4.06 (s, 10 H), 4.09 (s, 20 H), 4.32 (t, *J* = 1.9 Hz, 4 H), 4.35 (t, *J* = 1.9 Hz, 8 H), 4.68 (t, *J* = 1.9 Hz, 4 H), 4.71 (t, *J* = 1.9 Hz, 8 H), 6.88 (br. d, *J* = 8.2 Hz, 2 H), 7.12 (br. d, *J* = 8.2 Hz, 4 H), 7.32, (br. d, *J* = 8.2 Hz, 2 H), 7.44−7.50 (m, 10 H), 7.53 (t, *J* = 1.7 Hz, 1 H), 7.55 (t, *J* = 1.7 Hz, 2 H), 7.63 ppm (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 0.1, 66,65, 66.68, 69.28, 69.29, 69.82, 69.84, 84.47, 84.52, 88.9, 89.0, 90.4, 90.5, 95.7, 104.4, 121.5, 121.8, 122.9, 123.15, 123.20, 123.8, 123.9, 126.7, 126.8, 130.0, 131.2, 131.4, 131.7, 133.1, 138.7, 138.9, 139.76, 139.80, 140.9, 141.7 ppm; IR (ATR): $\tilde{\nu}$ = 2957 (w), 2160 (w), 1588 (s), 1507 (m), 1442 (m), 1411 (m), 1249 (m), 1106 (s), 1032 (m), 1000 (s), 816 cm^{-1} (s); HR-MALDI-MS (DCTB): *m*/*z* (%): 1804.2647 (27), 1805.2677 (37), 1806.2613 (81, *M*$^+$, calc. for $C_{113}H_{86}Fe_6Si^+$: 1806.2596), 1807.2628 (100), 1808.2655 (68), 1809.2681 (33), 1810.2706 (13).

1,2,3,-Tris{4-[2-(3,5-diferrocenylphenyl)ethynyl]phenyl}-5-ethynylbenzene (3). A solution of **19** (90 mg, 0.05 mmol) in MeOH/THF 1:1 (100 mL) was treated with K_2CO_3 (34 mg, 0.24 mmol), stirred at 25 °C for 2 h, diluted with CH_2Cl_2 (100 mL), and washed with H_2O (2 × 100 mL). Evaporation and flash chromatography (SiO2; hexane/CH_2Cl_2 1:1) gave **3** (77 mg, 89%) as an orange solid. R_f = 0.51 (SiO2; hexane/CH_2Cl_2 1:1); mp > 240 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.19 (s, 1 H), 4.06 (s, 10 H), 4.08 (s, 20 H), 4.32 (t, *J* = 1.8 Hz, 4 H), 4.35 (t, *J* = 1.8 Hz, 8 H), 4.68 (t, *J* = 1.8 Hz, 4 H), 4.70 (t, *J* = 1.8 Hz, 8 H), 6.88 (br. d, J = 8.2 Hz, 2 H), 7.12 (br. d, J = 8.3 Hz, 4 H), 7.32, (br. d, J = 8.2 Hz, 2 H), 7.44−7.50 (m, 10 H), 7.52 (t, J = 1.7 Hz, 1 H), 7.55 (t, J = 1.7 Hz, 2 H), 7.65 ppm (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 66.66, 66.69, 69.28, 69.30, 69.8, 69.9, 78.4, 83.1, 84.48, 84.53, 88.85, 88.93, 90.5, 90.6, 121.6, 121.87, 121.94, 123.1, 123.2, 123.86, 123.94, 126.75, 126.80, 130.0, 131.2, 131.4, 131.7, 133.3, 138.8, 139.1, 139.78, 139.81, 140.8, 141.8 ppm; IR (ATR): $\tilde{\nu}$ = 2924 (w), 2111 (w), 1589 (s), 1508 (w), 1442 (w), 1411 (w), 1252 (m), 1106 (s), 1032 (m), 1000 (s), 817 cm^{-1} (s); HR-MALDI-MS (DCTB): m/z (%): 1732.2244 (30), 1733.2273 (36), 1734.2210 (84, M^+, calc. for $C_{110}H_{78}Fe_6^+$: 1734.2201), 1735.2225 (100), 1736.2250 (63), 1737.2280 (28).

4,4′-[5-(3,3-Diethyltriaz-1-en-1-yl)-1,3-phenylene]bis(ethyne-2,1-diyl)bis(*N*,*N*-dihexylaniline) (24). A solution of **22** (511 mg, 1.19 mmol) in $i$$Pr_2NH$ (60 mL) was deoxygenated thoroughly by bubbling Ar for 30 min, treated with **23** (852 mg, 2.98 mmol), CuI (69 mg, 0.36 mmol), and $[PdCl_2(PPh_3)_2]$ (168 mg, 0.24 mmol), and stirred under Ar for 12 h. Evaporation and FC (SiO_2; hexane/CH_2Cl_2 3:1) gave **24** (752 mg, 85%) as a yellow solid. R_f = 0.15 (SiO_2; hexane/CH_2Cl_2 3:1); mp 90−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, J = 6.4 Hz, 12 H), 1.25−1.50 (m, 30 H), 1.50−1.65 (m, 8 H), 3.28 (t, J = 7.1 Hz, 8 H), 3.78 (q, J = 7.1 Hz, 4 H), 6.58 (br. d, J = 8.8 Hz, 4 H), 7.37 (br. d, J = 8.8 Hz, 4 H), 7.40 (t, J = 1.5 Hz, 1 H), 7.47 ppm (d, J = 1.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.2, 22.8, 27.0, 27.3, 31.9, 51.1, 87.1, 90.8, 109.0, 111.3, 122.6. 124.8, 130.6, 133.1, 148.0, 151.2 ppm (16 out of 18 signals expected); IR (ATR): $\tilde{\nu}$ = 2953 (m), 2926 (m), 2856 (m), 2201 (m), 1606 (s), 1583 (s), 1569 (s), 1517 (s), 1465 (m), 1401 (m), 1368 (m), 1251 (m), 1190 (m), 1105 (m), 811 cm^{-1} (m); HR-MALDI-MS (3-HPA): m/z (%) 744.1482 (100 $[M + H]^+$, calc. for $C_{50}H_{74}N_5^+$: 744.1481).

4,4′-(5-Iodo-1,3-phenylene)bis(ethyne-2,1-diyl)bis(*N*,*N*-dihexylaniline) (25). NaI (247 mg, 1.65 mmol) and Me_3SiCl (157 mg, 1.44 mmol) were added to a solution of triazene **24** (350 mg, 0.47 mmol) in MeCN (30 mL) and CCl_4 (10 mL). The mixture was stirred under Ar at 60 °C for 20 min. Sat. aq. $NaHCO_3$ solution (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. FC (SiO_2; hexane/CH_2Cl_2 4:1) gave **25** (156 mg, 43%) as a yellow oil. R_f = 0.41 (SiO_2; hexane/CH_2Cl_2 4:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.92 (t, J = 6.8 Hz, 12 H), 1.33 (br. s, 24 H), 1.50−1.65 (m, 8 H), 3.28 (t, J = 7.8 Hz, 8 H), 6.57 (br. d, J = 9.0 Hz, 4 H), 7.34 (br. d, J = 9.0 Hz, 4 H), 7.55 (t, J = 1.5 Hz, 1 H), 7.72 ppm (d, J = 1.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.2, 22.8, 27.0, 27.3, 31.9, 51.1, 85.3, 92.9, 93.3, 108.1, 111.3, 126.3, 133.0, 133.2, 138.4, 148.3 ppm; IR (ATR): $\tilde{\nu}$ = 2953 (m), 2924 (m), 2854 (m), 2200 (m), 1605 (s), 1576 (s), 1516 (s), 1465 (m), 1399 (m), 1366 (m), 1293 (m), 1190 (m), 1121 (m), 810 cm^{-1} (m); HR-MALDI-MS (3-HPA) m/z (%): 771.4116 (100, $[M + H]^+$, calc. for $C_{46}H_{64}N_2I^+$: 771.4109), 772.4148 (51), 773.4179 (12), 774.5137 (2).

4,4′-{5-[2-(Trimethylsilyl)ethynyl]-1,3-phenylene}bis(ethyne-2,1-diyl)bis(*N*,*N*-dihexylaniline) (26). A solution of **25** (700 mg, 0.91 mmol) in Et_3N (60 mL) was deoxygenated thoroughly by bubbling Ar through for 30 min. (Trimethylsilyl)-acetylene (257 μL, 1.82 mmol), CuI (10 mg, 0.05 mmol), and $[PdCl_2(PPh_3)_2]$ (23 mg, 0.03 mmol) were added, and the mixture was stirred under Ar for 14 h. Evaporation and FC (SiO_2; hexane/CH_2Cl_2 4:1) gave **26** (626 mg, 93%) as a yellow oil. R_f = 0.43 (SiO_2; hexane/CH_2Cl_2 4:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.25 (s, 9 H), 0.91 (t, J = 6.9 Hz, 12 H), 1.33 (br. s, 24 H), 1.50−1.65 (m, 8 H), 3.27 (t, J = 7.6 Hz, 8 H), 6.56 (br. d, J = 9.0 Hz, 4 H), 7.33 (br. d, J = 9.0 Hz, 4 H), 7.47 (d, J = 1.6 Hz, 2 H), 7.53 ppm (t, J = 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 0.1, 14.2, 22.8, 27.0, 27.3, 31.9, 51.1, 86.0, 92.0, 94.9, 104.1, 108.4, 111.3, 123.6, 124.9, 133.1, 133.3, 133.7, 148.2 ppm; IR (ATR): $\tilde{\nu}$ = 2955 (m), 2926 (m), 2856 (m), 2201 (m), 2151 (w), 1606 (s), 1574 (s), 1517 (s), 1465 (m), 1400 (m), 1367 (m), 1294 (m), 1249 (m), 1190 (m), 1119 (m), 973 (m), 842 (s) 811 cm^{-1} (s); HR-MALDI-MS (3-HPA): m/z (%): 741.5542 (100, $[M + H]^+$, calc. for $C_{51}H_{73}N_2Si^+$: 741.5538), 742.5576 (55), 743.5609 (14), 744.5643 (4).

4,4′-(5-Ethynyl-1,3-phenylene)bis(ethyne-2,1-diyl)bis(*N*,*N*-dihexylaniline) (27). A solution of **26** (670 mg, 0.9 mmol) in MeOH/THF 1:1 (120 mL) was treated with K_2CO_3 (0.72 g, 5.21 mmol), stirred at 25 °C for 2 h, diluted with CH_2Cl_2 (100 mL), and washed with H_2O (2 × 100 mL). Evaporation and flash chromatography (SiO2; hexane/CH_2Cl_2 3:1) gave **27** (587 mg, 97%) as a colorless oil. R_f = 0.45 (SiO_2; hexane/CH_2Cl_2 3:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, J = 6.6 Hz, 12 H), 1.33 (br. s, 24 H), 1.50−1.65 (m, 8 H), 3.07 (s, 1 H), 3.28 (t, J = 7.7 Hz, 8 H), 6.57 (br. d, J = 9.0 Hz, 4 H), 7.35 (br. d, J = 9.0 Hz, 4 H), 7.49 (d, J = 1.6 Hz, 2 H), 7.58 ppm (t, J = 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.2, 22.8, 27.0, 27.3, 31.9, 51.1, 77.7, 82.7, 85.9, 92.2, 108.3, 111.3, 122.6, 125.0, 133.1, 133.4, 134.1, 148.3 ppm; IR (ATR): $\tilde{\nu}$ = 3305 (w), 2953 (m), 2925 (m), 2855 (m), 2199 (w), 1606 (s), 1574 (s), 1516 (s), 1465 (m), 1399 (m), 1366 (m), 1293 (m), 1253 (m), 1190 (m), 1180 (m), 1120 (w), 960 (m), 875 (m) 810 cm^{-1} (s); HR-MALDI-MS (DCTB): m/z (%): 668.5065 (100, M^+, calc. for $C_{48}H_{64}N_2^+$: 668.5064), 669.5098 (50), 670.5131 (12).

3,3-Diethyl-1-[3,4,5-tris(4-{[3,5-bis(ethyne-2,1-diyl)bis(*N*,*N*-dihexylaniline)phenyl]-ethynyl}phenyl)phenyl]triaz-1-ene (28). A solution of **10** (175 mg, 0.22 mmol) in $i$$Pr_2NH$ (40 mL) and THF (20 mL) was deoxygenated thoroughly by bubbling Ar through for 30 min, treated with **27** (722 mg, 1.08 mmol), CuI (26 mg, 0.14 mmol), and $[PdCl_2(PPh_3)_2]$ (53 mg, 0.076 mmol), and stirred at 40 °C for 14 h. Evaporation and FC (SiO_2; hexane/CH_2Cl_2 3:1) gave **28** (274 mg, 51%) as an orange amorphous film. R_f = 0.12 (SiO_2; hexane/CH_2Cl_2 2:1); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 0.80−0.95 (m, 36 H), 1.24−1.42 (m, 78 H), 1.52−1.60 (m, 24 H), 3.22−3.36 (s, 24 H), 3.82 (q, J = 7.1 Hz, 4 H), 6.57−6.68 (m, 12 H), 6.91 (d, J = 8.2 Hz, 2 H), 7.16 (br. d, J = 8.3 Hz, 4 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.30−7.38 (m, 12 H), 7.40 (br. d, J = 8.3 Hz, 4 H), 7.47−7.56 ppm (m, 11 H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 14.4, 23.3, 27.3, 27.7, 32.3, 51.5, 86.3, 88.9, 89.0, 90.5, 90.7, 92.60, 92.64, 108.37, 108.40, 111.7, 121.1, 121.4, 122.2, 124.4, 125.51, 125.54, 130.6, 131.4, 131.6, 132.6, 133.1, 133.5, 134.1, 134.3, 135.3, 140.6, 142.5, 143.0, 148.8, 148.9, 151.2 ppm (37 out of 44 signals expected); IR (ATR): $\tilde{\nu}$ = 3044 (w), 2953 (m), 2929 (m), 2855 (m), 2199 (m), 1606 (s), 1574 (s), 1516 (s), 1464 (m), 1398 (m), 1366 (m), 1293 (m), 1252 (m), 1225 (w), 1190 (m), 1118 (w), 962 (m), 872 (m) 810 cm^{-1} (s); HR-MALDI-MS (DCTB): m/z (%): 2404.6943 (54, $[M + H]^+$, calc. for $C_{172}H_{214}N_9^+$: 2404.6938), 2405.6977 (100), 2406.7011 (96), 2407.7045 (61), 2408.7085 (27), 2409.7117 (11).

{5-[(Trimethylsilyl)ethynyl]-1,3-phenylene}bis(ethyne-2,1-diyl)ferrocene (33). A solution of **32** (1.79 g, 4.20 mmol) in $i$$Pr_2NH$ (100 mL) was deoxygenated thoroughly by bubbling Ar for 30 min. Ethynylferrocene (1.94 g, 9.23 mmol), CuI (160 mg, 0.84 mmol), and $[PdCl_2(PPh_3)_2]$ (295 mg, 0.42 mmol) were added, and the mixture was stirred under Ar for 12 h. Evaporation and FC (SiO_2; hexane/CH_2Cl_2 2:1) gave **33** (2.26 g, 91%) as a yellow solid. R_f = 0.52 (SiO_2; hexane/CH_2Cl_2 2:1); mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.26 (s, 9 H), 4.20−4.30 (m, 14 H), 4.49 (t, J = 1.9 Hz, 4 H), 7.51 (d, J = 1.6 Hz, 2 H), 7.53 ppm (t, J = 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 0.1, 64.8, 69.2, 70.2, 71.7, 84.5, 89.8, 95.4, 103.7, 123.8, 124.6, 133.7, 133.9 ppm; IR (ATR): $\tilde{\nu}$ = 3094 (m), 2957 (m), 2897 (m), 2218 (m), 2163 (m), 1581 (s), 1469 (w), 1411 (m), 1105 (m), 816 (s), 681 cm^{-1} (m); HR-MALDI-MS (DCTB) m/z (%): 588.0856 (13), 589.0893 (5), 590.0809 (100, M^+, calc. for $C_{35}H_{30}Fe_2Si^+$: 590.0811), 591.0846 (36), 592.0884 (6), 593.0814 (2).

(5-Ethynyl-1,3-phenylene)bis(ethyne-2,1-diyl)ferrocene (34). A solution of **33** (500 mg, 0.85 mmol) in MeOH/THF 1:1 (100 mL) was treated with K_2CO_3 (235 mg, 1.7 mmol), stirred at 25 °C for 2 h, diluted with CH_2Cl_2 (100 mL), and washed with H_2O (2 × 100 mL). Evaporation and FC (SiO2; hexane/CH_2Cl_2 1:1) gave **34** (417 mg, 95%) as a red solid. R_f = 0.71 (SiO_2; hexane/CH_2Cl_2 1:1); mp 188−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ =

3.09 (s, 1 H), 4.20–4.30 (m, 14 H), 4.50 (t, J = 1.9 Hz, 4 H), 7.52 (d, J = 1.6 Hz, 2 H), 7.57 ppm (t, J = 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 64.7, 69.2, 70.2, 71.7, 78.1, 82.4, 84.3, 90.0, 122.8, 124.8, 133.8, 134.3 ppm; IR (ATR): $\tilde{\nu}$ = 3094 (m), 2213 (s), 1581 (m), 1468 (w), 1411 (m), 1105 (m), 814 (s), 684 cm^{-1} (m); HR-MALDI-MS (DCTB) m/z (%) 516.0459 (13), 517.0496 (5), 518.0414 (100, M^+, calc. for $C_{32}H_{22}Fe_2^+$: 518.0416), 519.0448 (34), 520.0485 (5).

3,3-Diethyl-1-[3,4,5-tris(4-{[3,5-bis(ferrocenylethyne-2,1-diyl)phenyl]ethynyl}phenyl)phenyl]-triaz-1-ene (35). A solution of **10** (175 mg, 0.22 mmol) in iPr$_2$NH (40 mL) was deoxygenated thoroughly by bubbling Ar thorough for 30 min, **34** (496 mg, 0.96 mmol), CuI (18 mg, 0.095 mmol), and [PdCl$_2$(PPh$_3$)$_2$] (34 mg, 0.048 mmol) were added, and the mixture was stirred at 40 °C for 14 h. Evaporation, FC (SiO$_2$; hexane/CH$_2$Cl$_2$ 1:1) and recycling GPC (JAI 2H; CHCl$_3$) gave **35** (245 mg, 56%) as an orange solid. R_f = 0.25 (SiO$_2$; hexane/CH$_2$Cl$_2$ 1:1); mp > 147 °C (decomp); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.30 (t, J = 7.2 Hz, 6 H), 3.82 (q, J = 7.2 Hz, 4 H), 4.20–4.30 (m, 42 H), 4.45–4.55 (m, 12 H), 6.86 (br. d, J = 8.5 Hz, 2 H), 7.14 (br. d, J = 8.5 Hz, 4 H), 7.21, (br. d, J = 8.5 Hz, 2 H), 7.38 (br. d, J = 8.5 Hz, 4 H), 7.50–7.60 ppm (m, 11 H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 21.3, 47.6, 64.8, 69.11, 69.14, 70.2, 71.7, 84.5, 88.4, 88.5, 89.78, 89.81, 90.5, 90.7, 116.3, 120.5, 121.0, 121.9, 124.00, 124.02, 124.69, 124.72, 130.1, 131.0, 131.2, 132.0, 133.26, 133.29, 133.6, 135.0, 140.0, 142.0, 142.4, 150.7 ppm (34 out of 38 signals expected); IR (ATR): $\tilde{\nu}$ = 2931 (w), 2212 (m), 1579 (s), 1464 (m), 1444 (m), 1408 (m), 1331 (s), 1292 (w), 1242 (m), 1105 (s), 1042 (w), 1024 (m), 1001 (s), 821 (s), 731 cm^{-1} (s); HR-MALDI-MS (DCTB) m/z (%): 1951.3025 (26), 1952.30.44 (36), 1953.2987 (77), 1954.3005 (100, M^+, calc. for $C_{124}H_{87}Fe_6N_3^+$: 1954.3035), 1955.3026 (69), 1956.3060 (37), 1957.3086 (13).

1-[3,4,5-Tris(4-{[3,5-bis(ferrocenylethyne-2,1-diyl)phenyl]ethynyl}phenyl)iodophenyl (29). A solution of **35** (105 mg, 0.05 mmol) in MeI (5 mL) was deoxygenated thoroughly by bubbling Ar for 30 min, then stirred in a sealed tube at 120 °C for 16 h, and evaporated. FC (Al$_2$O$_3$; hexane/CH$_2$Cl$_2$ 2:1) gave **29** (91 mg, 85%) as an orange solid. R_f = 0.20 (SiO$_2$; hexane/CH$_2$Cl$_2$ 2:1); mp > 193 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 4.20–4.30 (m, 42 H), 4.46–4.52 (m, 12 H), 6.82 (br. d, J = 8.5 Hz, 2 H), 7.06 (br. d, J = 8.5 Hz, 4 H), 7.22, (br. d, J = 8.5 Hz, 2 H), 7.37 (br. d, J = 8.5 Hz, 4 H), 7.50–7.60 (m, 9 H), 7.82 ppm (s, 2 H); ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 64.8, 69.1, 69.2, 70.2, 71.7, 84.5, 88.8, 88.9, 89.8, 89.9, 90.1, 90.3, 93.5, 121.3, 121.7, 123.8, 123.9, 124.7, 124.8, 129.9, 131.2, 131.4, 131.6, 133.27, 133.30, 133.7, 133.8, 138.1, 138.5, 138.7, 140.3, 143.3 ppm (32 out of 36 signals expected); IR (ATR): $\tilde{\nu}$ = 3092 (w), 2923 (m), 2853 (m), 2211 (m), 1578 (s), 1410 (m), 1262 (m), 1192 (w), 1106 (m), 1024 (m), 1000 (m), 971 (m), 906 (s), 874 (s), 819 (s), 727 cm^{-1} (s); HR-MALDI-MS (DCTB) m/z (%): 1978.1234 (27), 1979.1255 (35), 1980.1194 (85, M^+, calc. for $C_{120}H_{77}Fe_6I^+$: 1980.1168), 1981.1208 (100), 1982.1230 (68), 1983.1255 (33), 1984.1281 (13).

Sonogashira Coupling of Ethyne 3 with Iodo Compound 29. A solution of **29** (20 mg, 0.01 mmol) in iPr$_2$NH (20 mL) and THF (40 mL) was deoxygenated thoroughly by bubbling Ar through for 30 min, **3** (18 mg, 0.01 mmol), CuI (1 mg, 0.005 mmol), and [PdCl$_2$(PPh$_3$)$_2$] (4 mg, 0.005 mmol) were added, and the mixture was stirred at 25 °C for 14 h. Evaporation and purification by recycling GPC (JAI 2H; CHCl$_3$) gave **36** (21 mg, 57%) and **37** (7 mg) as orange solids.

*Compound **36**.* R_f = 0.59 (SiO$_2$; hexane/CH$_2$Cl$_2$ 4:5); mp > 240 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 4.08 (s, 10 H), 4.10 (s, 20 H), 4.25–4.30 (m, 42 H), 4.34 (t, J = 1.9 Hz, 4 H), 4.37 (t, J = 1.9 Hz, 8 H), 4.51 (t, J = 1.9 Hz, 4 H), 4.52 (t, J = 1.9 Hz, 8 H), 4.70 (t, J = 1.9 Hz, 4 H), 4.72 (t, J = 1.9 Hz, 8 H), 6.90 (br. d, J = 8.5 Hz, 2 H), 6.94 (br. d, J = 8.5 Hz, 2 H), 7.15 (br. d, J = 8.5 Hz, 4 H), 7.19 (br. d, J = 8.5 Hz, 4 H), 7.27 (br. d, J = 8.5 Hz, 2 H), 7.36 (br. d, J = 8.5 Hz, 2 H), 7.43 (br. d, J = 8.5 Hz, 4 H), 7.48 (d, J = 1.7 Hz, 2 H), 7.49–7.52 (m, 8 H), 7.53–7.58 (m, 8 H) 7.59 (d, J = 1.6 Hz, 4 H), 7.73 (s, 2 H), 7.75 ppm (s, 2 H); ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 64.8, 66.67, 66.70, 69.1, 69.2, 69.3, 69.9, 70.2, 71.7, 84.50, 84.54, 88.77, 88.84, 88.9, 89.0, 89.8, 89.86, 89.90, 90.0, 90.2, 90.4, 90.45, 90.54, 121.2, 121.5, 121.8, 122.8, 122.9, 123.15, 123.20, 123.90, 123.93, 124.7, 124.8, 126.77, 126.81, 130.0, 130.1, 131.2, 131.4, 131.69, 131.73, 132.9, 133.0, 133.28, 133.31, 133.7, 138.6, 138.8, 138.9, 139.1, 139.78, 139.81, 140.9, 141.1, 141.8, 141.9 ppm; IR (ATR): $\tilde{\nu}$ = 3091 (m), 2926 (m), 2704 (w), 2210 (m), 1580 (s), 1507 (m), 1410 (m), 1253 (m), 1106 (s), 1000 (s), 873 (m), 817 (s), 730 cm^{-1} (m); UV/vis (CH$_2$Cl$_2$): λ_{max} (ε) = 294 (sh, 262000), 310 (273600), 445 nm (7600 M^{-1} cm^{-1}); HR-MALDI-MS (DCTB): m/z (%): 3583.4360 (16), 3584.4325 (32), 3585.4300 (56), 3586.4276 (82, M^+, calc. for $C_{230}H_{154}Fe_{12}^+$: 3586.4351), 3587.4258 (99), 3588.4268 (100), 3589.4305 (80), 3590.4339 (53), 3591.4370 (28), 3592.4404 (13).

*Compound **37**.* R_f = 0.68 (SiO$_2$; hexane/CH$_2$Cl$_2$ 4:5); mp > 235 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 4.06 (s, 20 H), 4.08 (s, 40 H), 4.32 (t, J = 1.8 Hz, 8 H), 4.35 (t, J = 1.9 Hz, 16 H), 4.68 (t, J = 1.8 Hz, 8 H), 4.70 (t, J = 1.9 Hz, 16 H), 6.89 (br. d, J = 8.6 Hz, 4 H), 7.14 (br. d, J = 8.6 Hz, 8 H), 7.33 (br. d, J = 8.6 Hz, 4 H), 7.45 (d, J = 1.7 Hz, 4 H), 7.46–7.50 (m, 16 H), 7.52 (t, J = 1.7 Hz, 2 H), 7.55 (t, J = 1.7 Hz, 4 H), 7.71 ppm (s, 4 H); ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 66.67, 66.70, 69.3, 69.8, 69.9, 75.1, 81.6, 84.48, 84.53, 88.8, 88.9, 90.55, 90.63, 121.5, 121.7, 122.0, 123.1, 123.2, 123.9, 124.0, 126.77, 126.81, 130.0, 131.2, 131.5, 131.6, 133.7, 138.7, 139.7, 139.79, 139.82, 140.6, 142.0; IR (ATR): $\tilde{\nu}$ = 3089 (m), 2953 (m), 2922 (m), 2852 (w), 2209 (m), 1582 (s), 1506 (m), 1410 (m), 1252 (m), 1105 (s), 1000 (s), 873 (m), 816 (s), 731 cm^{-1} (m); UV/vis (CH$_2$Cl$_2$): λ_{max} (ε) = 289 (240000), 311 (sh, 188000), 446 nm (4800 M^{-1} cm^{-1}); HR-MALDI-MS (DCTB): m/z (%): 3463.4357 (16), 3464.4381 (35), 3465.4381 (56), 3466.4343 (79, M^+, calc. for $C_{220}H_{154}Fe_{12}^+$: 3466.4350), 3467.4350 (100), 3468.4360 (98), 3469.4382 (80), 3470.4389 (50), 3471.4433 (25), 3472.4462 (11).

3,3′-(5-Ethynyl-1,3-phenylene)bis(2-(4-(dihexylamino)-phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile) (38). TCNE (38 mg, 0.30 mmol) was added to a solution of **27** (50 mg, 0.075 mmol) in dichloroethane (5 mL). The mixture was stirred under an Ar atmosphere. Evaporation and FC (SiO$_2$; CH$_2$Cl$_2$) gave **38** (61 mg, 89%) as a dark orange film. R_f = 0.60 (SiO$_2$; CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 0.92 (t, J = 6.8 Hz, 12 H), 1.29–1.40 (m, 24 H), 1.60–1.75 (m, 8 H), 3.34 (s, 1 H), 3.41 (t, J = 7.9 Hz, 8 H), 6.70 (br. d, J = 9.4 Hz, 4 H), 7.70 (br. d, J = 9.4 Hz, 4 H), 7.76 (t, J = 1.8 Hz, 1 H), 7.97 ppm (d, J = 1.8 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 14.1, 22.8, 26.8, 27.5, 31.7, 51.8, 72.3, 80.0, 83.1, 90.8, 110.6, 111.2, 112.9, 114.1, 114.4, 116.5, 126.3, 129.9, 132.8, 133.9, 135.9, 153.6, 160.2, 166.8 ppm; IR (ATR): $\tilde{\nu}$ = 2954 (m), 2927 (m), 2856 (m), 2213 (m), 2114 (w), 1601 (s), 1483 (s), 1445 (s), 1414 (s), 1339 (s), 1213 (m), 1183 (s), 823 (m), 638 cm^{-1} (m); UV/vis (CH$_2$Cl$_2$): λ_{max} (ε) = 298 (32000), 460 nm (59 700 M^{-1} cm^{-1}); HR-MALDI-MS (DCTB): m/z (%): 947.5206 (100 [M + Na]$^+$, calc. for $C_{60}H_{64}N_{10}Na^+$: 947.5208), 948.5244 (69), 949.5274 (24), 950.5322 (5).

3,3′-(5-Ethynyl-1,3-phenylene)bis(2-ferrocenylbuta-1,3-diene-1,1,4,4-tetracarbonitrile) (39). TCNE (99 mg, 0.77 mmol) was added to a solution of **34** (100 mg, 0.19 mmol) in dichloroethane, and the mixture was stirred at 80 °C for 6 h. Evaporation and purification by FC (SiO$_2$; CH$_2$Cl$_2$) gave a rotameric mixture of **39** (123 mg, 82%, (**39a**/**39b**: 5/3) as a dark green solid. R_f = 0.52 (SiO$_2$; CH$_2$Cl$_2$); mp 223–225 °C; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO, 25 °C): **39a**: δ = 4.12 (br. s, 1 H), 4.37 (s, 10 H), 4.93–5.00 (m, 4 H), 5.09–5.16 (m, 2 H), 5.31–5.36 (m, 2 H), 8.37 (d, J = 1.8 Hz, 2 H), 8.44 (t, J = 1.8 Hz, 1 H); **39b**: 4.12 (br. s, 1 H), 4.43 (s, 10 H), 4.88–4.92 (m, 2 H), 4.93–5.00 (m, 2 H), 5.09–5.16 (m, 2 H), 5.50–5.55 (m, 2 H), 8.16 (t, J = 1.8 Hz, 1 H), 8.37 (d, J = 1.8 Hz, 2 H); ^{13}C NMR (100 MHz, (CD$_3$)$_2$CO, 25 °C): δ = 72.1, 72.2, 73.4, 73.5, 74.5, 74.9, 75.0, 75.1, 76.6, 76.8, 77.5, 77.6, 80.1, 80.3, 80.9, 81.0, 84.6, 84.7, 91.8, 91.9, 112.39, 112.41, 112.5, 112.7, 114.78, 114.81, 115.0, 115.1, 126.8, 126.9, 129.2, 130.0, 135.0, 135.4, 136.7, 136.9, 163.5, 164.2, 170.9, 171.3 ppm; IR (ATR): $\tilde{\nu}$ = 2220 (m), 1520 (s), 1440 (m), 1413 (m), 1380 (w), 1329 (w), 1286 (w), 1171 (m), 1040 (w), 1004 (m), 835 (m), 795 cm^{-1} (m); UV/vis (CH_2Cl_2): λ_{max} (ε) = 308 (31000), 521 (sh, 1500), 638 nm (2900 M^{-1} cm^{-1}); HR-MALDI-MS (DCTB): m/z (%) 772.0710 (12), 773.0743 (6), 774.0660 (100 $[M + Na]^+$, calc. for $C_{44}H_{22}Fe_2N_8^+$: 774.0662), 775.0697 (48), 776.0732 (12), 777.0762 (3).

***Janus*-System 2.** TCNE (43 mg, 0.33 mmol) was added to a solution of **36** (100 mg, 0.03 mmol) in dichloroethane (5 mL), and the mixture was stirred at 80 °C for 6 h. Evaporation and FC (SiO_2; EtOAc) gave **2** (70 mg, 58%) as a dark green solid. R_f = 0.32 (SiO_2; EtOAc); mp > 300 °C; IR (ATR): $\tilde{\nu}$ = 2953 (m), 2322 (m), 1722 (w), 1590 (m), 1521 (m), 1456 (m), 1378 (m), 1172 (m), 1106 (s), 1002 (s), 833 cm^{-1} (m); UV/vis (CH_2Cl_2): λ_{max} (ε) = 296 (247000), 314 (251000) 507 (sh, 6500), 639 nm (10 000 M^{-1} cm^{-1}); HR-MALDI-MS (DCTB): m/z (%) 4351.5136 (12), 4352.5120 (24), 4353.5085 (43), 4354.5059 (65, M^+, calc. for $C_{266}H_{154}Fe_{12}N_{24}^+$: 4354.5090), 4355.5050 (89), 4356.5053 (100), 4357.5073 (89), 4358.5117 (65), 4359.5158 (39), 4360.5195 (21), 4361.5228 (9). For the ^1H and ^{13}C NMR spectra, see Figures S65 and S66 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra and electrochemistry of all new compounds; crystal structure data for compounds **9**, **10**, **33**, and **39**; rotamer formation analysis by NMR, GPC, and MS; and theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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