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## New Push-Pull Chromophores Featuring TCAQ (11,11,12,12-Tetracyano-9,10-anthraquinodimethane) and Other Dicyanovinyl Acceptors

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Stable, highly colored push-pull chromophores with NMe<sub>2</sub> donor and C=C(CN)<sub>2</sub> acceptor moieties, featuring intense intramolecular charge-transfer (CT) bands in the UV/Vis spectra, are reported. In an attempt to prepare the quinoid push-pull systems **2**, chromophores **10** and **11**, with a central cyclohexene spacer, were obtained and characterized by X-ray analysis. A series of donor-substituted TCAQ (11,11,12,12-tetracyano-9,10-anthraquinodimethane) derivatives were synthesized, using the Knoevenagel condensation between appropriately functionalized anthraquinones and malono-nitrile, mediated by the Lehnert reagent (TiCl<sub>4</sub>/pyridine), as the key step. HCl addition to triple bonds was observed

### Introduction

Push-pull chromophores, with the electron donor and acceptor separated by  $\pi$ -conjugating linkers (D– $\pi$ –A), have been investigated for decades.<sup>[1]</sup> Nevertheless, they continue to attract growing interest in view of their promising optoelectronic properties, in particular their second-order<sup>[2]</sup> and third-order<sup>[2a,3,4]</sup> nonlinear optical (NLO) behavior, and their potential for application as advanced functional materials in molecular devices.

We have prepared several families of new push-pull chromophores featuring intense, bathochromically shifted intramolecular charge-transfer (CT) bands, high third-order optical nonlinearities,<sup>[4]</sup> and interesting redox properties.<sup>[5]</sup> They comprise donor–acceptor-substituted tetraethynylethenes (TEEs, 3,4-diethynylhex-3-ene-1,5-diynes)<sup>[4,6]</sup> and D– $\pi$ –A systems featuring new potent electron acceptors, such as donor-substituted cyanoethynylethenes (CEEs)<sup>[7]</sup> and 1,1,4,4-tetracyano-1,3-butadienes (TCBDs).<sup>[8]</sup> In a when this transformation was applied to alkynylated anthraquinones. Electrochemical studies by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV) showed that introduction of donor substituents into the TCAQ core of **25**, **26**, and **31** shifts the first reduction potential to more negative values, while chromophores bearing guanidine moieties (**27**, **28**) displayed a specific and complex redox behavior. Both electrochemical and UV/Vis data provide good evidence that D-A conjugation is more efficient through olefinic (in **10**) than through acetylenic (in **37**) spacers.

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comprehensive study, we identified a strong dependence of ground-state D–A conjugation from the length of the  $\pi$ spacer. More efficient D-A conjugation leads to larger optical gaps.<sup>[7,9]</sup> Smaller optical gaps, i.e. more bathochromically shifted CT bands, are obtained by reducing the efficiency of D-A conjugation through introduction of extended spacers, such as alkenes or alkynes.<sup>[7,9]</sup> At strong D-A conjugation, the HOMO (highest occupied molecular orbital) of the donor is lowered and the LUMO (lowest unoccupied molecular orbital) of the acceptor raised, yielding a large optical (and electrochemical) gap. In the case of weaker D-A conjugation, i.e. when donor and acceptor are separated by larger spacers, the energy levels of HOMO and LUMO resemble those in the free components and a smaller optical gap (bathochromically shifted CT band) is measured. At the same time, the insertion of large  $\pi$  spacers was found to strongly enhance third-order optical nonlinearities of the push-pull chromophores.<sup>[4]</sup>

On the other hand, literature reports that D– $\pi$ –A compounds with  $\pi$  spacers, that gain aromaticity ("proaromatic" spacers) upon CT excitation,<sup>[1]</sup> yield low-energy CT transitions and large first molecular hyperpolarizabilities  $\beta^{[10]}$  In 1968, Gompper et al. described the first such chromophore 1, with a strong 1,3-dithio-2-ylidene donor and a strong dicyanomethylene acceptor,<sup>[11]</sup> and since then, a variety of D– $\pi$ –A systems with quinoid  $\pi$  spacers and low-energy CT transitions have been prepared.<sup>[10a,12]</sup>



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We have now started an experimental program aimed at merging these two approaches towards achieving low-energy CT absorptions and high NLO efficacies. Here, we describe our attempts to prepare the new quinoid push-pull systems 2 (n = 0, 1). We also report on the synthesis and electronic properties of a series of donor-substituted 11,11,12,12-tetracyano-9,10-anthraquinodimethane

 $(TCAQ)^{[13,14]}$  derivatives with the general structure **3** (Figure 1). While several such compounds are known,<sup>[15]</sup> the number of systematic investigations of D– $\pi$ –A systems with TCAQ as acceptor remains limited.



Figure 1. Quinoid push-pull chromophores 1,<sup>[11b]</sup> 2, and 3.

### **Results and Discussion**

### Attempted Synthesis of Push-Pull Chromophores 2

On the way to **2** (n = 0, 1), dibromoolefination of commercially available 1,4-dioxaspiro[4.5]decan-8-one furnished **4** (Scheme 1).<sup>[16]</sup> Removal of the acetal protecting group<sup>[17]</sup> and subsequent Sonogashira<sup>[18]</sup> or Suzuki<sup>[19]</sup> cross-coupling on **5**, using 4-ethynyl-*N*,*N*-dimethylaniline or [4-(dimeth-



ylamino)phenyl]boronic acid,<sup>[20]</sup> afforded donor-substituted cyclohexanones 6 and 7, respectively. Al<sub>2</sub>O<sub>3</sub>-catalyzed Knoevenagel condensation<sup>[21]</sup> with malononitrile smoothly provided 8 and 9 in good yields. Oxidation of the central cyclohexane moiety was accomplished using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at 20 °C.<sup>[18]</sup> Surprisingly, only the blue, stable cyclohexene derivatives 10 and 11, instead of the quinoid chromophores 2 (n = 0, 1), were formed and isolated (Scheme 1). All further attempts to prepare 2 also failed: various oxidation conditions [excess of DDQ or reflux,<sup>[18]</sup> MnO<sub>2</sub>,<sup>[22a]</sup> ceric ammonium nitrate (CAN),<sup>[22b]</sup> NH<sub>4</sub>NO<sub>3</sub>/trifluoroacetic anhydride (TFAA)<sup>[22c]</sup>] only yielded insoluble polymers, presumably featuring poly(p-xylylene) backbones similar to those obtained from homopolymerization of other quinodimethane-type monomers.<sup>[23]</sup>

X-ray analysis [see Supporting Information (SI)] confirmed the proposed structures of 10 and 11, with their incompletely oxidized central cyclohexene ring (Figure 2). In compound 10, the entire  $\pi$ -conjugated chromophore, including the two N,N-dimethylanilino (DMA) rings, is planar, with a maximum out-of-plane deviation of 0.28 Å (N31). The crystal packing shows a layered structure with a distance of 3.27 Å between the mean planes of molecules in neighboring layers (shortest interatomic distance C6…C14 3.39 Å). In contrast, the DMA rings in 11 are forced out of the mean plane passing through the divinylcyclohexene ring to avoid repulsive intramolecular contacts, as already seen in previous work.<sup>[9]</sup> The DMA ring adjacent to the bulkier CH<sub>2</sub> group is turned out somewhat more (torsional angle C1-C2-C9-C10 46°) than the other DMA ring (C1–C2–C3–C4 41°).



Scheme 1. Synthesis of push-pull chromophores **10** and **11**. (a) CBr<sub>4</sub>, PPh<sub>3</sub>, benzene,  $\Delta$ , 12 h, 68%; (b) CH<sub>3</sub>COOH, H<sub>2</sub>O, 75 °C, 2 h, 99%; (c) for **6**: 4-ethynyl-*N*,*N*-dimethylaniline, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], CuI, Et<sub>3</sub>N, 20 °C, 48 h, 89%; for **7**: 4-(dimethylamino)phenylboronic acid, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], Na<sub>2</sub>CO<sub>3</sub>, THF, H<sub>2</sub>O, 70 °C, 12 h, 87%; (d) (CN)<sub>2</sub>CH<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>,  $\Delta$ , 1 h, 93% (**8**, **9**); (e) DDQ, toluene, 20 °C, 1 h, 42% (**10**), 50% (**11**). DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.



Figure 2. ORTEP representations of compounds 10 (a) and 11 (b). Vibrational ellipsoids obtained at 202–203 K are shown at the 50% probability level (for further information, see SI).

#### Synthesis of TCAQ-Based D-A Chromophores

TCAQ and derivatives are conveniently accessible by Knoevenagel condensation of anthracene-9,10-dione derivatives with malononitrile, mediated by TiCl<sub>4</sub>/pyridine (Lehnert reagent).<sup>[24]</sup> Therefore, our efforts were focused on the preparation of various donor-substituted anthracene-9,10-diones, starting from commercially available 2-aminoand 2,6-diaminoanthracene-9,10-diones **12** and **13** (Scheme 2). *N*-Methylation using MeI/KOH/Me<sub>2</sub>SO readily furnished anthraquinones **14** and **15**, respectively, in good yields.<sup>[25]</sup> Treatment of **12** or **13** with N,N,N',N'-tetramethylurea in the presence of phosphoryl chloride (POCl<sub>3</sub>)<sup>[26]</sup> afforded the N,N,N',N'-tetramethylguanidine derivatives **16** and **17**, respectively. Diazotation of **12**, followed by substitution with iodide, afforded 2-iodoanthracene-9,10-dione (**18**).<sup>[27]</sup> A similar transformation of **13** furnished an inseparable mixture of products. On the other hand, diazotization with *tert*-butyl nitrite, followed by Sandmeyer reaction with CuBr<sub>2</sub>, gave 2,6-dibromoanthracene-9,10-dione (**19**).<sup>[28]</sup> Facile Sonogashira or Suzuki cross-coupling on **18** afforded DMA-substituted anthraquinones **20** and **21**, respectively,



Scheme 2. Synthesis of donor-substituted anthracene-9,10-diones. (a) KOH, Me<sub>2</sub>SO, 20 °C, 30 min, then CH<sub>3</sub>I, 20 °C, 10 min, 95% (14), 87% (15); (b) *N*,*N*,*N'*,*N'*-tetramethylurea, POCl<sub>3</sub>, benzene, 20 °C, 12 h, then 12 or 13,  $\Delta$ , 6 h, 52% (16), 23% (17); (c) 18: THF, H<sub>2</sub>O, HCl, 40 °C, 24 h, then NaNO<sub>2</sub>/H<sub>2</sub>O, 0 °C, 10 min and KI/H<sub>2</sub>O, 0 °C, 15 min  $\rightarrow$  20 °C, 30 min  $\rightarrow$  60 °C, 30 min, 81%; 19: *t*BuONO, CuBr<sub>2</sub>, CH<sub>3</sub>CN, 65 °C, 2 h, 91%; (d) 20: [4-(dimethylamino)phenyl]boronic acid, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], Na<sub>2</sub>CO<sub>3</sub>, THF, H<sub>2</sub>O, 60 °C, 1 h, 96%; 21/22: 4-ethynyl-*N*,*N*-dimethylaniline, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], CuI, Et<sub>3</sub>N/Et<sub>2</sub>NH, 20 °C/ $\Delta$ , 5 min/12 h, 97% (21), 45% (22); 23: 4-ethynyl-*N*,*N*-dihexylaniline, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], CuI, Et<sub>2</sub>NH,  $\Delta$ , 12 h, 76%.

in nearly quantitative yields. Also, dibromo derivative **19** underwent smoothly a twofold Sonogashira cross-coupling furnishing **22**. Due to the low solubility of **22**, its *N*,*N*-dihexyl analogue **23** was synthesized as well (Scheme 2).

The Knoevenagel reaction with malononitrile, mediated by the Lehnert reagent, was first carried out on unsubstituted anthracene-9,10-dione, yielding TCAQ (24) in 89% yield. The other, donor-substituted anthraquinones were treated with malononitrile under the above condition as well. Whereas anthraquinones 14-17 and 20 afforded the expected products 25-28 and 31, respectively, derivatives bearing a triple-bond linker between the DMA and the anthraquinone moieties (21-23) were hydrochlorinated, yielding products 32-34 (Scheme 3). The regioselectivity of the HCl addition is controlled by the potency of the DMA moiety to stabilize a carbocationic intermediate. The (Z)configuration of 32 was proven by X-ray analysis (see below). Modification of the reaction conditions did also not lead to the desired alkynes; dehydrohalogenations proved to be difficult as well. In an alternative approach, the Knoevenagel condensation was carried out on 18 and 19, provid-



Scheme 3. TiCl<sub>4</sub>-mediated Knoevenagel condensation. Reaction conditions: reflux, 36–96 h.



Scheme 4. Synthesis of  $D-\pi-D$  system **36**. (a) CBr<sub>4</sub>, PPh<sub>3</sub>, benzene, 20 °C, 24 h, 96%; (b) 4-ethynyl-*N*,*N*-dimethylaniline, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], CuI, benzene, Et<sub>2</sub>NH, 20 °C, 48 h, 9%.



ing 2-iodinated (29) and 2,6-dibrominated (30)<sup>[13c]</sup> TCAQs. However, Sonogashira or Suzuki cross-coupling reactions of 29 and 30 were not successful and, therefore, the products with triple-bond linkers were not synthesized. On the other hand starting from the tetrabromide 35, fourfold Sonogashira coupling could be successfully applied to the synthesis of the new extended D– $\pi$ –D system 36, which was obtained as a red solid in low yield (9%; Scheme 4).

X-ray crystal structures were obtained for the two anthraquinones 17 and 20 and the two TCAQ derivatives 25 and 32, confirming the proposed structures (Figure 3).

a)



Figure 3. ORTEP representations of the compounds (a) **17** (223 K), (b) **20** (203 K), (c) **25** (223 K; mean dihedral angle between the plane through the cyanovinyl group and the planes through the two phenyl rings  $37 \pm 2^{\circ}$ , dihedral angle between the two phenyl ring planes  $34^{\circ}$ ), and (d) **32** (203 K; mean dihedral angle between the plane through the cyanovinyl group and the planes through the two phenyl rings  $42 \pm 2^{\circ}$ , dihedral angle between the two phenyl ring planes  $34^{\circ}$ ). Vibrational ellipsoids are shown at the 50% probability level (for further information, see SI).

N21

The crystal structure of 20 contains two symmetrically independent molecules which arrange in a herringbone pattern with an interplanar angle of 42°. The C=O dipoles of two neighboring, symmetry-independent molecules undergo favorable orthogonal C=O····C=O interactions (distance O····C 3.3 Å, angle C····C=O 108°).<sup>[29]</sup> The structures of 25 and 32 show the typical, saddle-like out-of-plane deformation,<sup>[15c,30]</sup> reported for TCAQ derivatives, which is induced by steric hindrance between the C(CN)<sub>2</sub> moieties and the tricyclic central core. The chloroethene derivative 32 is (Z)-configured, as expected for an *anti*-HCl addition to the intermediate alkyne. On the basis of spectral similarity (NMR, UV, IR), we also assume this double-bond configuration for compounds 33 and 34. An (E) configuration would lead to sterically repulsive interactions between DMA and C(CN<sub>2</sub>) moieties. It should also be noted that the (Z) geometry in 32 induces a favorable Cl···CN interactions (angle C-Cl···N 103°, distance Cl···N 3.62 Å), also referred to as halogen bonding.[31]

#### Electrochemistry

Electrochemical investigations were carried out by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in  $CH_2Cl_2 + 0.1 \text{ M} nBu_4NPF_6$ , using the ferricinium/ferrocene (Fc<sup>+</sup>/Fc) couple as internal reference (Table 1). TCAQ (**24**) had previously been studied by Aumüller and Hünig<sup>[13a]</sup> and Gerson and co-workers.<sup>[14c]</sup> In contrast to 7,7,8,8-tetra-cyanoquinodimethane (TCNQ),<sup>[32]</sup> TCAQ is reduced in a single reversible two-electron step. The peak characteristics in acetonitrile clearly demonstrate that a potential inversion for the two overlapping one-electron transfers occurs.

Under our experimental conditions, namely in dichloromethane, the peak characteristics are in agreement with a normal ordering of the two overlapping one-electron reduction steps, indicative of two almost independent redox centers, as suggested by Gerson and co-workers.

For most compounds, well-resolved voltammograms could be observed. However, for some species such as 27 and 28, electrode inhibition required electrode polishing between each scan. The reduction of TCAQ derivatives 24-28 and 32-34 occurs in a single, unresolved reversible twoelectron step. The peak characteristics show that the peak potentials are scan-rate-independent and that the peak-potential difference for the first reduction step ranges from 90 to 100 mV. This indicates that the two reversible one-electron transfers are separated by about 80 mV. The difference in redox behavior between TCNQ (2 distinct one-electron reductions) and TCAO (unresolved two-electron step) reflects differences in the electronic communication between the two dicyanovinyl redox centers. Whereas this communication is high in planar TCNQ, it is much reduced in TCAQ derivatives due to nonplanarity of the chromophore (see the X-ray crystal structures of 25 and 32 in Figure 3) and, most importantly, the reduction in  $\pi$  conjugation between the two redox centers as a result of double benzene-ring fusion to the quinodimethane scaffold.

Table 1. Electrochemical data obtained by cyclic voltammetry (CV) at a scan rate of  $0.1 \text{ V s}^{-1}$  and rotating disk voltammetry (RDV) in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> (vs. Fc<sup>+</sup>/Fc).

Compound	Cyclic voltametry			Rotating disk voltametry	
	$E^{\circ}$ [V] <sup>[a]</sup>	$\Delta E_{\rm p}  [{\rm mV}]^{[{\rm b}]}$	$E_{\rm p}  [V]^{[c]}$	$E_{1/2}  [V]^{[d]}$	Slope [mV] <sup>[e]</sup>
10			+0.48	[f]	
	-1.31	100		-1.35	65
			$-1.75^{[f]}$	-1.81 <sup>[g]</sup>	65
	-2.29	100			
11	+0.70	80			
			+0.32	+0.33	50
			-1.71 <sup>[h]</sup>	-1.45	
24	-0.81	100		-0.84 (2 e <sup>-</sup> )	90
25	+0.93	110		+0.92 (1 e <sup>-</sup> )	75
	-0.90	170		-0.97 (2 e <sup>-</sup> )	90
26			+1.00		
			+0.88	0.85 (1 e <sup>-</sup> )	60
	-0.98	90		-1.00 (2 e <sup>-</sup> )	50
27			+0.72		
			+0.44		
	-0.73	70		-0.80 (1 e <sup>-</sup> )	
	-0.88	100		–0.99 (2 e <sup>–</sup> )	
	-1.05	60		-1.14 (1 e <sup>-</sup> )	
	-1.42	60		–1.53 (1 e <sup>–</sup> )	
28	-0.86	70			
	-0.95	110		Electrode	
	-1.40	80		inhibition	
	-1.58	130			
31	+0.51	75		+0.52 (1 e <sup>-</sup> )	70
	-0.82	100		–0.85 (2 e <sup>–</sup> )	75
32			+0.46	+0.43 (1 e <sup>-</sup> )	50
	-0.79	100		–0.83 (2 e <sup>–</sup> )	60
33			+0.45		
	-0.79	90		–0.82 (2 e <sup>–</sup> )	50
34			+0.43	+0.41 (2 e <sup>-</sup> )	60
	-0.77	160		–0.84 (2 e <sup>–</sup> )	60
36	+0.59	115			
			+0.27	+0.17	100
			-1.73	[1]	
<b>37</b> <sup>[j]</sup>			+0.43	+0.40	
			-1.24	-1.18	70
			-1.74	-1.68	70

[a]  $E^{\circ} = (E_{\rm pc} + E_{\rm pa})/2$ , where  $E_{\rm pc}$  and  $E_{\rm pa}$  correspond to the cathodic and anodic peak potentials, respectively. [b]  $\Delta E_{\rm p} = E_{\rm ox} - E_{\rm red}$ , where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [c]  $E_{\rm p}$  = Irreversible peak potential. [d]  $E_{1/2}$  = Half-wave potential. [e] Slope of the linearized plot of *E* vs. log[*I*/( $I_{\rm lim} - I$ )], where  $I_{\rm lim}$  is the limiting current and *I* the current. [f] Adsorption peak. [g] Strong adsorption post wave. [h] Reversible at scan rates higher than 2 V s<sup>-1</sup>. [i] Unresolved spread out reduction wave. [j] Taken from ref.<sup>[9]</sup>



The observed reduction potentials are dependent of the nature of the substituents.  $NMe_2$  substituents directly attached to the TCAQ core (25, 26) are stronger electron-donating (negative potential shift of the first reduction wave of 90 mV per substituent) than DMA residues (31; negative

potential shift of only 10 mV). In contrast, upon introduction of the chlorovinyl spacers in **32–34**, the first reduction step becomes facilitated (shift to more positive potential by 20–40 mV as compared to TCAQ). DMA and DHA moieties in **31–34** undergo reversible one-electron oxidations between +0.43 and +0.51 V, as previously observed.<sup>[5]</sup>

The guanidine derivatives **27** and **28** show a specific redox behavior. Indeed, **27** gives four well-resolved reversible electron transfers at -0.73, -0.88, -1.05, and -1.42 V, respectively. The first, third, and fourth reduction step involve a one-electron transfer, whereas the second reduction involves a two-electron transfer which may occur on the two C=C(CN)<sub>2</sub> moieties. For the disubstituted species **28**, the rotating disk voltammograms are not well resolved due to adsorption phenomena; nevertheless, four reductions are observed by cyclic voltammetry.

Finally, in view of the actual debate about the efficiency of double and triple bonds in transmitting conjugative effects,<sup>[33]</sup> a comparison between the chromophores **10** (Scheme 1) and previously reported **37** (below Table 1)<sup>[9]</sup> seems worthwhile. The two D– $\pi$ –A systems contain identical donor and acceptor moieties and differ only by the central section of the  $\pi$  linker, namely (*Z*)-ethenediyl in **10**  and ethynediyl in **37**. Ground-state D–A conjugation is substantially stronger in **10**, with the olefinic spacer, than in **37**, with the acetylenic spacer. The DMA moiety in **10** is more difficult to oxidize (+0.48 V) than in **37** (+0.43 V) and, accordingly, the dicyanovinyl acceptor in **10** is also more difficult to reduce (-1.31 V) than in **37** (-1.24 V). The electrochemical gap  $\Delta(E_{\text{ox},1} - E_{\text{red},1})$  in **10** is -1.79 V whereas it amounts to -1.67 V in **37**. Obviously, some (minor) influence of the bridging ethanediyl fragment in the cyclohexene ring on the redox potentials for **10** cannot be excluded.

#### **UV/Vis Spectroscopy**

UV/Vis spectroscopic data of the new chromophores were recorded in CH<sub>2</sub>Cl<sub>2</sub> and are summarized in Table 2. The more effective D–A conjugation in ethenediyl-linked **10**, as compared to ethynediyl-linked **37**, is also apparent from the higher energy of the intramolecular CT band and the larger optical gap in the UV/Vis spectra:  $\lambda_{max} = 528$  nm (2.35 eV) and  $\lambda_{end} = 699$  nm (1.77 eV) for **10** and  $\lambda_{max} = 534$  nm (2.32 eV) and  $\lambda_{end} = 740$  nm (1.68 eV) for **37**.



Figure 4. UV/Vis spectra of the TCAQ derivatives 24-28 and 31 in CH<sub>2</sub>Cl<sub>2</sub>.



Figure 5. UV/Vis spectra of TCAQ derivatives 32–34 and D– $\pi$ –D system 36 in CH<sub>2</sub>Cl<sub>2</sub>.

Table 2. Longest-wavelength absorptions and end-absorptions in  $CH_2Cl_2$  determined by UV/Vis spectroscopy.

Compound	$\lambda_{\rm max} \ [{\rm nm} \ ({\rm eV})]$	$\lambda_{end} [nm (eV)]$
10	528 (2.35)	699 (1.77)
11	531 (2.33)	665 (1.86)
24	347 (3.57)	406 (3.05)
25	553 (2.24)	664 (1.87)
26	588 (2.11) <sup>[a]</sup>	669 (1.85)
27	524 (2.37)	679 (1.83)
28	480 (2.58)	610 (2.03)
31	571 (2.17)	748 (1.66)
32	549 (2.26)	710 (1.75)
33	544 (2.28)	734 (1.69)
34	580 (2.14)	766 (1.62)
36	486 (2.55)	576 (2.15)
<b>37</b> <sup>[b]</sup>	534 (2.32)	740 (1.68)

[a] Peak fitting by Gaussian deconvolution of the broad absorption band of **26** gave a hidden peak maximum (observed as shoulder on the broad absorption) at  $\lambda_{max} = 588$  nm (2.11 eV). [b] Taken from ref.<sup>[9]</sup>

All TCAQ derivatives feature strong absorptions in the range between 250 and 380 nm, which are transitions involving the anthraquinodimethane core [compare the spectrum of TCAQ (24) in Figure 4]. In tetra(DMA-ethynyl)-substituted 36, additional strong bands at  $\lambda_{max} = 486$  and 576 nm are observed, reflecting an intramolecular CT from the peripheral donors into the tetraalkynylated anthraquinodimethane core (Figure 5).

Bathochromically shifted intramolecular CT bands are observed for all donor-substituted TCAQ derivatives (Figure 4), including the chlorovinyl derivatives **32–34** (Figure 5); they all form highly colored solids. The most intense CT bands are seen in the spectrum of bis(Me<sub>2</sub>N)-substituted TCAQ **26**, which also features the longest-wavelength absorption of all push-pull systems ( $\lambda_{max} = 588$  nm). The CT character of the longest-wavelength absorption of all push-pull chromophores was confirmed by protonation/ neutralization experiments (SI). Upon protonation of the Me<sub>2</sub>N groups with trifluoroacetic acid (TFA), all CH<sub>2</sub>Cl<sub>2</sub> solutions turned from intensely colored to nearly colorless and the longest-wavelength absorption bands disappeared almost completely. Full regeneration of the original CT bands occurred upon neutralization with Et<sub>3</sub>N.

#### Conclusions

A series of thermally stable D–A chromophores, featuring dialkylamino donors and dicyanovinyl acceptors, were prepared and their properties investigated. The initially targeted quinodimethane systems **2** were not obtained, due to ready polymerization, and the blue chromophores **10** and **11**, with a central cyclohexene spacer, were isolated and characterized instead. A variety of donor-substituted TCAQ derivatives were synthesized by Knoevenagel condensation of the appropriately substituted anthracene-9,10diones and malononitrile, mediated by the Lehnert reagent. However, this reagent (TiCl<sub>4</sub>/pyridine; used in excess) was found to be incompatible with alkyne linkers since the triple bonds were hydrochlorinated. X-ray crystal structures confirmed the saddle or butterfly conformation of TCAQ derivatives 25 and 32 as well as the configuration of the (Z)ethenediyl linker in 32. The UV/Vis spectra of the stable colored compounds feature intense CT bands with maxima in the range from 528 to 531 nm for 10 and 11 and from 480 to 580 nm for donor-substituted TCAQs 25-36, respectively. Very weak CT absorptions are observed for guanidine derivatives 27 and 28 which also show a rather complex redox behavior, featuring four reversible reduction steps. The electrochemical reductions of TCAOs 24-28 and 32–34 were observed in a single, unresolved reversible twoelectron step. Introduction of NMe2 and DMA chromophores (25, 26, 31) shifts the first reduction potential to more negative values, whereas the potential is shifted to more positive values in chromophores 32-34 bearing chlorovinyl spacers. This is in agreement with previous findings that introduction of larger spacers reduces the efficiency of D-A conjugation but also reflects the electronic effects of both substituents (NMe<sub>2</sub> vs. Cl). The comparison of electrochemical and UV/Vis data between 10, with a central ethenediyl, and previously prepared 37, with a central ethynediyl spacer, suggests that ground-state D-A conjugation across the olefinic spacer is more efficient – a finding of interest in view of the ongoing debate on the efficiency of olefinic versus acetylenic  $\pi$  conjugation. The third-order optical nonlinearities of the new chromophores are now investigated.

### **Experimental Section**

Materials and General Methods: Reagents and solvents were purchased at reagent grade from Acros, Aldrich, and Fluka, and used as received. THF was freshly distilled from Na/benzophenone under N<sub>2</sub>. Evaporation and concentration in vacuo was performed at water-aspirator pressure. All reactions were performed under a positive pressure of N<sub>2</sub>. Column chromatography (CC) and plug filtrations were carried out with SiO<sub>2</sub> 60 (particle size 0.040-0.063 mm, 230-400 mesh; Fluka) and distilled technical solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO<sub>2</sub> 60 F<sub>254</sub> obtained from Macherey-Nagel; visualization with a UV lamp (254 or 366 nm). Melting points (M.p.) were measured with a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected, "dec." refers to decomposition. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a Varian Gemini 300 spectrometer at 20 °C. Chemical shifts are reported in ppm relative to the signal of Me<sub>4</sub>Si. Residual solvent signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra were used as an internal reference. Coupling constants (J) are given in Hz. The apparent resonance multiplicity is described as s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), and m (multiplet). Anthraquinone protons are marked as AQ. Infrared spectra (IR) were recorded with a Perkin-Elmer Spectrum BX instrument. UV/ Vis spectra were recorded with a Varian Cary-5 spectrophotometer. The spectra were measured in  $CH_2Cl_2$  in a quartz cuvette (1 cm). The absorption wavelengths are reported in nm with the molar extinction coefficient  $\varepsilon$  (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) in parentheses; shoulders are indicated as sh. High-resolution (HR) EI-MS spectra were measured with a Hitachi-Perkin-Elmer VG-Tribrid spectrometer. HR FT-MALDI spectra were measured with an IonSpec Ultima Fourier transform (FT) instrument with [(2*E*)-3-(4-*tert*-butylphenyl)-2methylprop-2-enylidene]malononitrile (DCTB) or 3-hydroxypicolinic acid (3-HPA) as matrix. The most important signals are reported in *m*/*z* units with M as the molecular ion. [4-(Dimethylamino)phenyl]boronic acid was synthesized from 4-bromo-*N*,*N*dimethylaniline, according to a literature procedure, in 61% yield.<sup>[20]</sup> 4-Ethynyl-*N*,*N*-dimethylaniline and 4-ethynyl-*N*,*N*-dihexylaniline were prepared from 4-iodo-*N*,*N*-dimethylaniline or 4iodo-*N*,*N*-dihexylaniline and trimethylsilylacetylene by Sonogashira cross-coupling and final Me<sub>3</sub>Si group removal (K<sub>2</sub>CO<sub>3</sub>, MeOH) in 92% and 78% overall yields, respectively. Compounds 4 (68%),<sup>[16]</sup> 5 (99%),<sup>[17]</sup> 14 (95%),<sup>[25]</sup> 15 (87%),<sup>[25]</sup> 18 (81%),<sup>[27]</sup> 19 (91%),<sup>[28]</sup> 24 (89%),<sup>[15b]</sup> 25 (91%),<sup>[13b]</sup> 26 (66%),<sup>[13c]</sup> 30 (61%),<sup>[13c]</sup> and 35 (96%)<sup>[18,34]</sup> were prepared according to literature procedures in the indicated yields.

**Electrochemistry:** Electrochemical measurements were carried out in  $CH_2Cl_2$  containing 0.1 M  $nBu_4NPF_6$  in a classical three-electrode cell by cyclic voltammetry (CV) and rotating disk voltammetry (RDV). The working electrode was a glassy carbon disk (3 mm in diameter), the auxiliary electrode a platinum wire, and the reference electrode either an aq. Ag/AgCl reference electrode or a platinum wire used as pseudo-reference electrode. The cell was connected to an Autolab PGSTAT20 potentiostat (Eco Chemie, Holland) driven by a GPSE software running on a personal computer. All potentials are given versus Fc<sup>+</sup>/Fc used as internal reference and uncorrected from ohmic drop.

X-ray Analysis: CCDC-640603 (10), -640604 (11), -640608 (17), -640605 (20), -640606 (25), and -640607 (32) contain the supplementary crystallographic data for the new compounds reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request.cif. See also SI.

4-{1,5-Bis[4-(dimethylamino)phenyl]penta-1,4-diyn-3-ylidene}cyclohexanone (6): 4-Ethynyl-N,N-dimethylaniline (455 mg, 3.135 mmol) in triethylamine (50 mL), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (53 mg, 0.075 mmol) and CuI (28 mg, 0.149 mmol) were added to a degassed solution of the dibromo olefin 5 (400 mg, 1.493 mmol). The mixture was stirred under N<sub>2</sub> at 20 °C for 48 h. The solvent was evaporated in vacuo and the residue purified by CC [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane (2:1) to CH<sub>2</sub>Cl<sub>2</sub>]. Yield 527 mg (89%) as a brown solid.  $R_{\rm f} = 0.22$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane, 2:1); m.p. 181-182 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.52 (t, <sup>3</sup> $J_{H,H}$  = 6.9 Hz, 4 H, CH<sub>2</sub>), 2.98 (s, 12 H, NCH<sub>3</sub>), 3.02 (t,  ${}^{3}J_{H,H}$  = 6.9 Hz, 4 H, CH<sub>2</sub>), 6.63 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar), 7.37 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar) ppm.  ${}^{13}C$  NMR  $(75 \text{ MHz}, \text{CDCl}_3, 25 \text{ °C})$ :  $\delta = 29.49, 39.49, 40.27, 83.69, 93.43,$ 102.45, 109.73, 111.68, 132.54, 149.98, 150.10, 211.11 ppm. IR (neat):  $\tilde{v} = 2896$ , 2191, 1706, 1606, 1520, 1445, 1363, 1346, 1102, 1067, 943, 812 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 338 nm (sh, 46300 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for [C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sup>+</sup>] 397.2274; found 397.2274 [MH<sup>+</sup>].

**4-{Bis[4-(dimethylamino)phenyl]methylene}cyclohexanone (7):** [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (43 mg, 0.061 mmol) and Na<sub>2</sub>CO<sub>3</sub> (193 mg, 1.818 mmol) were added to a degassed solution of the dibromo olefin **5** (163 mg, 0.606 mmol) and [4-(dimethylamino)phenyl]boronic acid (300 mg, 1.818 mmol) in THF/H<sub>2</sub>O (10 mL, 4:1). The mixture was stirred under N<sub>2</sub> at 70 °C for 12 h, diluted with H<sub>2</sub>O, and extracted with EtOAc (2×50 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and concentrated in vacuo. Subsequent CC (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) afforded **7** (184 mg, 87%) as a yellow solid.  $R_{\rm f}$  = 0.23 (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 145–146 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.44 (t, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 4 H, CH<sub>2</sub>), 2.69 (t, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 4 H, CH<sub>2</sub>), 2.94 (s, 12 H, NCH<sub>3</sub>), 6.66 (d, <sup>3</sup>J<sub>H,H</sub> =



9.0 Hz, 4 H, Ar), 7.02 (d,  ${}^{3}J_{H,H} = 9.0$  Hz, 4 H, Ar) ppm.  ${}^{13}C$  NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 30.47$ , 40.62, 41.77, 111.75, 130.16, 130.42, 130.94, 138.13, 148.97, 212.37 ppm. IR (neat):  $\tilde{v} = 2886$ , 2797, 1709, 1606, 1516, 1442, 1337, 1225, 1190, 1164, 1129, 1061, 946, 821, 744 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 282 nm (28500 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): *m/z* calcd. for [C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sup>+</sup>] 349.2274; found 349.2268 [MH<sup>+</sup>].

2-(4-{1,5-Bis[4-(dimethylamino)phenyl]penta-1,4-diyn-3-ylidene}cyclohexylidene)malononitrile (8): Ketone 6 (50 mg, 0.126 mmol), malononitrile (9 mg, 0.139 mmol), and Al<sub>2</sub>O<sub>3</sub> (10 mg, 0.098 mmol, activity II-III) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were heated to reflux for 1 h. The mixture was filtered, concentrated in vacuo, and subjected to CC (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) yielding 8 (52 mg, 93%) as a brown solid.  $R_f =$ 0.79 (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 247–248 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.83–2.94 (m, 8 H, CH<sub>2</sub>), 2.98 (s, 12 H, NCH<sub>3</sub>), 6.66 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar), 7.35 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 31.11, 33.97, 40.27, 83.51, 84.04, 94.02, 102.98, 109.25, 111.82, 111.87, 132.68, 148.37, 150.53, 182.97 ppm. IR (neat):  $\tilde{v} = 2905$ , 2228, 2186, 1610, 1528, 1443, 1377, 1355, 1229, 1196, 1188, 1106, 983, 813, 799, 744 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ ) = 336 (40100), 293 nm  $(32400 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ . HR-FT-MALDI-MS (3-HPA): m/z calcd. for [C<sub>30</sub>H<sub>29</sub>N<sub>4</sub><sup>+</sup>] 445.2387; found 445.2380 [MH<sup>+</sup>].

**2-(4-{Bis[4-(dimethylamino)phenyl]methylene}cyclohexylidene)**malononitrile (9): The title compound was prepared from ketone 7 (100 mg, 0.287 mmol), according to the method described for 8. Yield 106 mg (93%) as a yellow solid.  $R_{\rm f} = 0.44$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 199–200 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 2.61$  (t, <sup>3</sup> $J_{\rm H,H} = 6.9$  Hz, 4 H, CH<sub>2</sub>), 2.77 (t, <sup>3</sup> $J_{\rm H,H} = 6.9$  Hz, 4 H, CH<sub>2</sub>), 2.95 (s, 12 H, NCH<sub>3</sub>), 6.66 (d, <sup>3</sup> $J_{\rm H,H} = 9.0$  Hz, 4 H, Ar), 6.97 (d, <sup>3</sup> $J_{\rm H,H} = 9.0$  Hz, 4 H, Ar) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 32.06$ , 35.57, 40.57, 82.83, 111.71, 128.59, 130.25, 130.41, 139.26, 149.14, 184.57 (1 C missing) ppm. IR (neat):  $\tilde{v} = 2887$ , 2795, 2230, 1607, 1517, 1441, 1343, 1218, 1190, 1165, 1124, 1055, 941, 826, 811, 749 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  ( $\varepsilon$ ) = 281 nm (35200 mol<sup>-1</sup>dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA):*m*/*z* calcd. for [C<sub>26</sub>H<sub>29</sub>N<sub>4</sub><sup>+</sup>] 397.2387; found 397.2381 [MH<sup>+</sup>].

2-(4-{1,5-Bis[4-(dimethylamino)phenyl]penta-1,4-diyn-3-ylidene}cyclohex-2-enylidene)malononitrile (10): To a solution of 8 (55 mg, 0.124 mmol) in dry toluene (20 mL), DDQ (42 mg, 0.186 mmol) was added. The violet mixture was stirred at 20 °C for 1 h, concentrated in vacuo, and subjected to CC (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) yielding 10 (23 mg, 42%). Metallic solid.  $R_f = 0.82$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. > 400 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.90–3.00 (m, 4 H, CH<sub>2</sub>), 3.02 (s, 6 H, NCH<sub>3</sub>), 3.03 (s, 6 H, NCH<sub>3</sub>), 6.66 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 4 H, Ar), 6.75 (d,  ${}^{3}J_{H,H}$  = 9.5 Hz, 1 H, CH), 7.42 (d,  ${}^{3}J_{\text{H,H}} = 9.0 \text{ Hz}, 4 \text{ H}, \text{ Ar}), 7.62 \text{ (d, } {}^{3}J_{\text{H,H}} = 9.5 \text{ Hz}, 1 \text{ H}, \text{ CH}) \text{ ppm.}$ <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 25.67, 28.57, 40.17, 78.59, 84.38, 86.84, 99.22, 102.55, 108.42, 108.48, 2×111.59, 111.99, 112.43, 113.28, 122.92, 133.02, 133.21, 140.90, 141.20, 150.49, 150.63, 167.69 ppm. IR (neat):  $\tilde{v} = 2850$ , 2162, 16001, 1520, 1486, 1351, 1305, 1218, 1184, 1097, 940, 810 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}(\varepsilon) = 528 \text{ (35200)}, 311 \text{ nm (sh, 36900 mol^{-1} dm^3 cm^{-1})}. \text{ HR-FT-}$ MALDI-MS (3-HPA):m/z calcd. for  $[C_{30}H_{26}N_4^+]$  442.2152; found 442.2157 [M<sup>+</sup>].

**2-(4-{Bis[4-(dimethylamino)phenyl]methylene}cyclohex-2-enylidene)**malononitrile (11): The title compound was synthesized from 9 (100 mg, 0.252 mmol), according to the method described for 10. Yield 49 mg (50%) as a metallic solid.  $R_{\rm f} = 0.6$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 150–151 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 2.81$  (s, 4 H, CH<sub>2</sub>), 3.02 (s, 6 H, NCH<sub>3</sub>), 3.03 (s, 6 H, NCH<sub>3</sub>), 6.55 (d, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz, 1 H, CH), 6.64 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 4 H, Ar), 6.99 (d,

 ${}^{3}J_{\text{H,H}} = 9.0 \text{ Hz}, 2 \text{ H}, \text{ Ar}), 7.01 (d, {}^{3}J_{\text{H,H}} = 9.5 \text{ Hz}, 1 \text{ H}, \text{ CH}), 7.07 (d, {}^{3}J_{\text{H,H}} = 9.0 \text{ Hz}, 2 \text{ H}, \text{ Ar}) \text{ ppm.} {}^{13}\text{C} \text{ NMR} (75 \text{ MHz}, \text{ CDCl}_3, 25 °\text{C}): \delta = 29.41, 29.84, 40.30, 73.93, 110.92, 113.25, 114.07, 119.78, 126.90, 127.94, 128.56, 132.30, 133.30, 147.54, 150.32, 150.78, 153.16, 169.04 \text{ ppm. IR} (neat): \tilde{v} = 2887, 2212, 1609, 1521, 1440, 1352, 1334, 1304, 1223, 1188, 1167, 1124, 1056, 947, 812 \text{ cm}^{-1}. \text{ UV/Vis} (\text{CH}_2\text{Cl}_2): \lambda_{\text{max}} (\varepsilon) = 531 (\text{sh}, 28500); 323 (\text{sh}, 14300), 287 \text{ nm} (20600 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}). \text{HR-FT-MALDI-MS} (3-\text{HPA}): m/z \text{ calcd. for } [\text{C}_{26}\text{H}_{26}\text{N}_4^+] 394.2152; \text{ found } 394.2146 [\text{M}^+].$ 

2-[4-(Dimethylamino)phenyl]anthracene-9,10-dione (20): [PdCl<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub>] (64 mg, 0.09 mmol) and Na<sub>2</sub>CO<sub>3</sub> (160 mg, 1.5 mmol) were added to a degassed solution of 18 (300 mg, 0.898 mmol) and [4-(dimethylamino)phenyl]boronic acid (248 mg, 1.5 mmol) in THF/ H<sub>2</sub>O (30 mL, 4:1). The mixture was stirred under N<sub>2</sub> at 60 °C for 1 h, diluted with H<sub>2</sub>O, and extracted with  $CH_2Cl_2$  (2 × 50 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and concentrated in vacuo. Subsequent CC [SiO2; CH2Cl2/hexane (1:1) to CH2Cl2] afforded **20** (282 mg, 96%) as an orange solid.  $R_{\rm f} = 0.45$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1); m.p. 233–234 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.04 (s, 6 H, NCH<sub>3</sub>), 6.81 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 2 H, Ar), 7.68 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 2 H, Ar), 7.75–7.85 (m, 2 H, AQ), 7.97 (dd,  ${}^{3}J_{H,H} = 9.0$ ,  ${}^{4}J_{H,H} = 2.0$  Hz, 1 H, AQ), 8.29–8.35 (m, 3 H, AQ), 8.49 (d,  ${}^{4}J_{H,H}$  = 2.0 Hz, 1 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): *δ* = 40.35, 112.38, 123.80, 125.86, 126.99, 127.05, 127.92, 130.64, 133.55, 133.66, 133.74, 133.90, 146.63, 150.73, 182.61, 183.37 (3 C missing) ppm. IR (neat):  $\tilde{v} = 2895$ , 1665, 1584, 1532, 1368, 1326, 1294, 1219, 1107, 1060, 951, 933, 911, 858, 818, 807, 731, 706, 696, 632 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>  $(\varepsilon) = 470 \ (8300), \ 362 \ (11900), \ 323 \ (17600), \ 255 \ nm \ (sh,$  $35500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ). HR-FT-MALDI-MS (3-HPA): m/z calcd. for [C<sub>22</sub>H<sub>17</sub>NO<sub>2</sub><sup>+</sup>] 327.1254; found 327.1249 [M<sup>+</sup>].

2-{[4-(Dimethylamino)phenyl]ethynyl}anthracene-9,10-dione (21): 4-Ethynyl-N,N-dimethylaniline (232 mg, 1.6 mmol) was added to a degassed solution of 18 (500 mg, 1.496 mmol), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (53 mg, 0.076 mmol), CuI (29 mg, 0.15 mmol), and Et<sub>3</sub>N (0.5 mL) in THF (10 mL). The deep red mixture was stirred at 20 °C for 5 min, then concentrated in vacuo. CC [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) to CH<sub>2</sub>Cl<sub>2</sub>] furnished **21** (510 mg, 97%) as a red solid.  $R_{\rm f} = 0.4$ (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1); m.p. 209-210 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.02 (s, 6 H, NCH<sub>3</sub>), 6.68 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 2 H, Ar), 7.45 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 2 H, Ar), 7.75–7.86 (m, 3 H, AQ), 8.26 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 1 H, AQ), 8.30–8.35 (m, 2 H, AQ), 8.37 (d,  ${}^{4}J_{H,H}$  = 2.0 Hz, 1 H, AQ) ppm.  ${}^{13}C$  NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 40.02, 86.84, 96.62, 108.57, 111.62, 127.11, 127.16, 127.23, 129.51, 130.67, 131.36, 133.13, 133.30, 133.37, 133.56, 133.92, 134.10, 135.83, 150.52, 182.42, 182.76 ppm. IR (neat):  $\tilde{v} = 2894$ , 2186, 1670, 1661, 1612, 1585, 1529, 1369, 1335, 1317, 1281, 1237, 1198, 1168, 1068, 931, 861, 806, 707, 633 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\varepsilon$ ) = 462 (10700), 362 (17300), 326 (26500), 286 (26800), 264 nm (33800 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for  $[C_{24}H_{17}NO_2^+]$  351.1254; found 351.1257  $[M^+].$ 

**2,6-Bis{[4-(dimethylamino)phenyl]ethynyl}anthracene-9,10-dione** (**22):** [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (58 mg, 0.082 mmol) and CuI (16 mg, 0.082 mmol) were added to a degassed solution of **19** (300 mg, 0.817 mmol) and 4-ethynyl-*N*,*N*-dimethylaniline (261 mg, 1.803 mmol) in Et<sub>2</sub>NH (50 mL). The mixture was heated to reflux under N<sub>2</sub> for 12 h and afterwards concentrated in vacuo. Subsequent CC [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) to CH<sub>2</sub>Cl<sub>2</sub>] afforded **22** (182 mg, 45%) as a dark red solid.  $R_{\rm f} = 0.13$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1); m.p. > 400 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 3.03$  (s, 12 H, NCH<sub>3</sub>), 6.68 (d, <sup>3</sup>*J*<sub>H,H</sub> = 9.0 Hz, 4 H, Ar), 7.46 (d, <sup>3</sup>*J*<sub>H,H</sub> = 9.0 Hz, 4 H, Ar), 7.83 (dd,  ${}^{3}J_{\text{H,H}}$  = 9.0,  ${}^{4}J_{\text{H,H}}$  = 2.0 Hz, 2 H, AQ), 8.26 (d,  ${}^{3}J_{\text{H,H}}$  = 9.0 Hz, 2 H, AQ), 8.37 (d,  ${}^{4}J_{\text{H,H}}$  = 2.0 Hz, 2 H, AQ) ppm.  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 40.19, 111.65, 130.24, 130.84, 133.11, 133.21, 135.71 (low solubility, 7 C missing) ppm. IR (neat):  $\tilde{v}$  = 2893, 2194, 1663, 1606, 1580, 1523, 1363, 1332, 1305, 1279, 1229, 1200, 1168, 1062, 815, 742, 712 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}} (\varepsilon)$  = 467 (20400), 375 (35400), 332 (34700), 289 (34200), 275 nm (35700 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): *m/z* calcd. for [C<sub>34</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>] 494.1989; found 494.1982 [M<sup>+</sup>].

2,6-Bis{[4-(dihexylamino)phenyl]ethynyl}anthracene-9,10-dione (23): The title compounds was synthesized from 18 (204 mg, 0.558 mmol) and 4-ethynyl-N,N-dihexylaniline (350 mg, 1.226 mmol) in a similar manner to **22**. Yield 264 mg (61%).  $R_{\rm f} = 0.45$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1); m.p. 160–161 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.91 (t, <sup>3</sup>J<sub>H,H</sub> = 6.5 Hz, 12 H, Hex), 1.30–1.38 (m, 24 H, Hex), 1.54–1.64 (m, 8 H, Hex), 3.28 (t,  ${}^{3}J_{H,H} = 7.5$  Hz, 8 H, Hex), 6.56 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar), 7.37 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar), 7.78 (dd,  ${}^{3}J_{H,H}$  = 9.0,  ${}^{4}J_{H,H}$  = 2.0 Hz, 2 H, AQ), 8.23 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 2 H, AQ), 8.32 (d,  ${}^{4}J_{H,H}$  = 2.0 Hz, 2 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.17, 22.79, 26.88, 27.26, 31.78, 51.00, 86.89, 97.11, 107.35, 111.06, 127.17, 129.35, 130.81, 131.14, 133.29, 133.42, 135.53, 148.38, 181.99 ppm. IR (neat):  $\tilde{v} = 2924, 2192, 1660, 1607, 1580, 1529, 1402, 1364, 1333,$ 1282, 1199, 1169, 849, 810, 741, 712 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>  $(\varepsilon) = 489 (23300), 385 (40400), 337 (38400), 295 (36300), 274 \text{ nm}$  $(37700 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ . HR-FT-MALDI-MS (3-HPA): m/z calcd. for [C<sub>54</sub>H<sub>67</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>] 775.5197; found 775.5209 [MH<sup>+</sup>].

TiCl<sub>4</sub>/Pyridine-Catalyzed Knoevenagel Condensation. General Method: Malononitrile (59.4 mg, 0.9 mmol), TiCl<sub>4</sub> (0.18 mL, 0.9 mmol), and pyridine (0.15 mL, 1.8 mmol) were added to an an-thracene-9,10-dione derivative (0.3 mmol) in CHCl<sub>3</sub> (50 mL), and the mixture was heated to reflux for the indicated time. Every 12 h, identical amounts of malononitrile, TiCl<sub>4</sub>, and pyridine were added. The mixture was poured on ice/water and extracted with CHCl<sub>3</sub> (3 × 100 mL). The combined organic layers were dried (MgSO<sub>4</sub>), concentrated in vacuo, washed with Et<sub>2</sub>O to remove excess of malononitrile, and subjected to CC.

2-[9,10-Bis(dicyanomethylene)-9,10-dihydroanthracen-2-yl]-1,1,3,3tetramethylguanidine (27): The title compound was prepared from 16 (100 mg, 0.311 mmol), according to the general method. The mixture was heated to reflux for 96 h, poured on ice/water, neutralized with NaHCO<sub>3</sub>, and extracted with  $CH_2Cl_2$  (3 × 100 mL). Subsequent CC (SiO<sub>2</sub>; acetone) afforded 27 (93 mg, 72%) as a dark solid.  $R_{\rm f} = 0.35$  (SiO<sub>2</sub>; acetone); m.p. 126–127 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.84 (s, 12 H, NCH<sub>3</sub>), 6.88 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0,  ${}^{4}J_{\text{H,H}}$  = 2.0 Hz, 1 H, AQ), 7.35 (d,  ${}^{4}J_{\text{H,H}}$  = 2.0 Hz, 1 H, AQ), 7.62–7.70 (m, 2 H, AQ), 8.09 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 1 H, AQ), 8.13– 8.16 (m, 1 H, AQ), 8.22-8.25 (m, 1 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): *δ* = 39.92, 82.02, 113.35, 113.38, 114.24, 114.38, 118.95, 124.44, 127.14, 127.20, 129.29, 130.21, 140.00, 131.47, 131.83, 132.04, 157.60, 159.98, 161.42, 161.79 (2 C missing) ppm. IR (neat):  $\tilde{v} = 2931, 2220, 1502, 1457, 1388, 1335, 1279, 1140,$ 1021, 835, 766, 697 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 524 (6830), 349 (sh, 20900), 285 nm (23400 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for  $[C_{25}H_{20}N_7^+]$  418.1775; found 418.1782 [MH<sup>+</sup>].

2',2'-[9,10-Bis(dicyanomethylene)-9,10-dihydroanthracene-2,6-diyl]bis(1,1,3,3-tetramethylguanidine) (28): The title compound was prepared from 17 (100 mg, 0.230 mmol), according to the general method. The mixture was heated to reflux for 96 h, poured on ice/ water, neutralized with NaHCO<sub>3</sub>, and extracted with CH<sub>2</sub>Cl<sub>2</sub>



 $(3 \times 100 \text{ mL})$ . Subsequent CC (Al<sub>2</sub>O<sub>3</sub>; CH<sub>2</sub>Cl<sub>2</sub>/acetone, 5:1) afforded **28** (25 mg, 21%) as a dark orange solid.  $R_{\rm f} = 0.65$  (Al<sub>2</sub>O<sub>3</sub>; CH<sub>2</sub>Cl<sub>2</sub>/acetone, 5:1); m.p. 129–130 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 2.83$  (s, 24 H, NCH<sub>3</sub>), 6.83 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.0, <sup>4</sup>J<sub>H,H</sub> = 2.0 Hz, 2 H, AQ), 7.36 (d, <sup>4</sup>J<sub>H,H</sub> = 2.0 Hz, 2 H, AQ), 8.00 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 2 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 39.89$ , 111.48, 114.59, 114.75, 118.85, 121.09, 123.76, 128.96, 132.61, 157.24, 161.20, 161.81 ppm. IR (neat):  $\tilde{v} = 2931$ , 2091, 1634, 1505, 1463, 1390, 1321, 1292, 1142, 1023, 834 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 480 (3800), 395 (5200), 347 (6600), 285 nm (9400 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for [C<sub>30</sub>H<sub>31</sub>N<sub>10</sub><sup>+</sup>] 531.2728; found 531.2730 [MH<sup>+</sup>].

2,2'-{2-[4-(Dimethylamino)phenyl]anthracene-9,10-diylidene}dimalononitrile (31): The title compound was prepared from 20 (100 mg, 0.31 mmol), according to the general method. The mixture was heated to reflux for 48 h. Yield 124 mg (96%), dark green solid.  $R_{\rm f} = 0.7$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 316–317 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.06 (s, 6 H, NCH<sub>3</sub>), 6.81 (d,  ${}^{3}J_{H,H}$ = 9.0 Hz, 2 H, Ar), 7.61 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 2 H, Ar), 7.70–7.75 (m, 2 H, AQ), 7.87 (dd,  ${}^{3}J_{H,H} = 9.0$ ,  ${}^{4}J_{H,H} = 2.0$  Hz, 1 H, AQ), 8.21–8.30 (m, 3 H, AQ), 8.39 (d,  ${}^{4}J_{H,H}$  = 2.0 Hz, 1 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 40.12, 81.13, 82.74, 112.49, 113.15, 113.40, 113.50, 124.60, 124.85, 126.18, 127.45, 128.10, 128.17, 128.76, 130.11, 130.48, 130.64, 132.11, 132.34, 145.59, 151.13, 160.03, 160.91 ppm (2 C missing). IR (neat):  $\tilde{v} = 2852$ , 2217, 1581, 1531, 1464, 1367, 1330, 1277, 1201, 1171, 1125, 950, 896, 814, 775, 731, 692 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 571 (7000), 422 (9800), 345 (27300), 308 (27400), 287 nm (31400 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for [C<sub>28</sub>H<sub>18</sub>N<sub>5</sub><sup>+</sup>] 422.1400; found 422.1400 [MH<sup>+</sup>].

(Z)-2,2'-(2-{2-Chloro-2-[4-(dimethylamino)phenyl]vinyl}anthracene-9,10-divlidene)dimalononitrile (32): The title compound was prepared from 21 (100 mg, 0.29 mmol), according to the general method. The mixture was heated to reflux for 72 h. Yield 121 mg (88%), dark blue solid.  $R_{\rm f} = 0.75$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 290–291 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): *δ* = 3.05 (s, 6 H, NCH<sub>3</sub>), 6.71 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 2 H, Ar), 7.63 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 2 H, Ar), 7.71–7.76 (m, 2 H, AQ), 8.02 (dd,  ${}^{3}J_{H,H} = 9.0$ ,  ${}^{4}J_{H,H} = 2.0$  Hz, 1 H, AQ), 8.20–8.28 (m, 3 H, AQ), 8.61 (d,  ${}^{4}J_{H,H}$  = 2.0 Hz, 1 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 40.38, 82.14, 83.37, 111.71, 113.109, 113.38, 113.54, 118.93, 125.28, 127.73, 127.78, 127.83, 128.29, 130.53, 130.57, 130.63, 132.52, 132.63, 132.94, 133.66, 138.44, 141.11, 151.58, 159.99, 160.67 ppm (3 C missing). IR (neat):  $\tilde{v} = 2811, 2222, 1574, 1537, 1520, 1341, 1327, 1169, 813,$ 767, 695 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 549 (8400), 351 (sh, 37000), 296 nm (27500 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for  $[C_{30}H_{19}ClN_5^+]$  484.1324; found 484.1321 [MH<sup>+</sup>].

**2,2'-(2,6-Bis{(Z)-2-chloro-2-[4-(dimethylamino)phenyl]vinyl}anthracene-9,10-diylidene)dimalononitrile (33):** The title compound was prepared from **22** (50 mg, 0.1 mmol), according to the general method. The mixture was heated to reflux for 96 h. Yield 53 mg (79%), dark solid.  $R_{\rm f} = 0.7$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 302–303 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 3.04$  (s, 12 H, NCH<sub>3</sub>), 6.71 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 4 H, Ar), 6.98 (s, 2 H, CH), 7.63 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 4 H, Ar), 8.02 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.0, <sup>4</sup>J<sub>H,H</sub> = 2.0 Hz, 2 H, AQ), 8.23 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 2 H, AQ), 8.61 (d, <sup>4</sup>J<sub>H,H</sub> = 2.0 Hz, 2 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 40.26$ , 81.96, 111.44, 113.15, 113.38, 118.77, 125.09, 127.38, 127.50, 127.72, 127.98, 130.50, 132.45, 137.98, 140.70, 151.20, 159.90 ppm. IR (neat):  $\tilde{v} = 2893$ , 2223, 1575, 1519, 1346, 1315, 1190, 1164, 1118, 911, 815, 803, 696, 625 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 544 (16900), 416 (29000), 353 (44700), 320 nm (43600 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for  $[C_{40}H_{28}Cl_2N_6^+]$  662.1747; found 662.1736 [M<sup>+</sup>].

2,2'-(2,6-Bis{(Z)-2-chloro-2-[4-(dihexylamino)phenyl]vinyl}anthracene-9,10-diylidene)dimalononitrile (34): The title compound was prepared from 23 (100 mg, 0.13 mmol), according to the general method. The mixture was heated to reflux for 48 h. Yield 83 mg (68%), dark green solid.  $R_{\rm f} = 0.9$  (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 77–78 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 0.91$  (t, <sup>3</sup> $J_{H,H} = 6.5$  Hz, 12 H, Hex), 1.30-1.40 (m, 24 H, Hex), 1.53-1.66 (m, 8 H, Hex), 3.32 (t,  ${}^{3}J_{H,H}$  = 7.5 Hz, 8 H, Hex), 6.63 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar), 6.95 (s, 2 H, CH), 7.60 (d,  ${}^{3}J_{H,H}$  = 9.0 Hz, 4 H, Ar), 8.00 (dd,  ${}^{3}J_{H,H} = 9.0, {}^{4}J_{H,H} = 2.0 \text{ Hz}, 2 \text{ H}, \text{ AQ}), 8.21 \text{ (d, } {}^{3}J_{H,H} = 9.0 \text{ Hz}, 2 \text{ Hz}, 2 \text{ Hz}$ H, AQ), 8.59 (d,  ${}^{4}J_{H,H}$  = 2.0 Hz, 2 H, AQ) ppm. <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{CDCl}_3, 25 \text{ °C}): \delta = 14.16, 22.77, 26.86, 27.27, 31.77,$ 51.10, 81.78, 110.87, 113.19, 113.45, 118.13, 123.89, 127.36, 127.50, 127.52, 128.17, 130.51; 132.32, 138.07, 140.82, 149.11, 159.94 ppm. IR (neat): v = 2925, 2222, 1578, 1547, 1515, 1366, 1294, 1254, 1183, 1117, 807 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 580 (18400), 438 (30200), 357 (47300), 327 nm (43700 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): *m*/*z* calcd. for [C<sub>60</sub>H<sub>69</sub>Cl<sub>2</sub>N<sub>6</sub><sup>+</sup>] 943.4955; found 943.4938 [MH+].

4,4',4'',4'''-[3,3'-(Anthracene-9,10-divlidene)bis(penta-1,4-divne-1,5-diyl-3-ylidene)]tetrakis(N,N-dimethylaniline) (36): To a degassed solution of 35 (260 mg, 0.5 mmol), 4-ethynyl-N,N-dimethylaniline (508 mg, 3.5 mmol), and Et<sub>2</sub>NH (0.3 mL, 3.0 mmol) in anhydrous benzene (15 mL), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (17.5 mg, 0.05 mmol) and CuI (4 mg, 0.02 mmol) were added. The mixture was stirred under N<sub>2</sub> at 20 °C for 2 d, concentrated in vacuo, and subjected to CC (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1 to 3:1). Yield 35 mg (9%), red solid.  $R_{\rm f} = 0.1$ (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 170–171 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.99 (s, 24 H, NCH<sub>3</sub>), 6.64 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 8 H, Ar), 7.34–7.37 (m, 4 H, AQ), 7.40 (d, J = 9.0 Hz, 8 H, Ar), 8.47– 8.50 (m, 4 H, AQ) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 40.26, 88.25, 94.78, 101.41, 110.28, 111.68, 126.27, 127.22, 132.71, 134.87, 142.46, 149.95 ppm. IR (neat):  $\tilde{v} = 2850, 2165, 1601, 1516$ , 1440, 1343, 1190, 1165, 1111, 1061, 944, 810, 764, 676 cm<sup>-1</sup>. UV/ Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 486 (29900), 400 (38700), 308 (sh, 46400), 250 nm (36800 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). HR-FT-MALDI-MS (3-HPA): m/z calcd. for [C<sub>56</sub>H<sub>48</sub>N<sub>4</sub><sup>+</sup>] 776.3874; found 776.3869 [M<sup>+</sup>].

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and spectral characterization of the compounds 16, 17, 25, 26, 29, and 30. X-ray crystallography data of the compounds 10, 11, 17, 20, 25, and 32. Representative CV diagrams as well as UV/Vis spectra.

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