DOI: 10.1002/ejoc.200801199

Preparation of an Indolylfulgimide-Adamantane Linker Conjugate with Nitrile Anchoring Groups through Palladium-Catalyzed Transformations

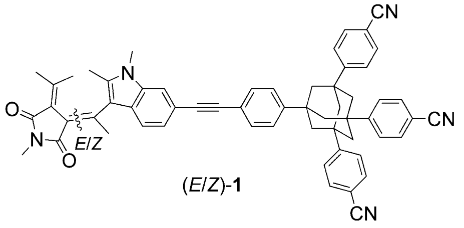
Sebastian Zarwell,[a] Steffen Dietrich,[a] Christine Schulz,[a] Paul Dietrich,[a] Fabian Michalik,[a] and Karola Rück-Braun*[a]

Keywords: Fulgimides / Photochromism / Tripods / Cross-coupling / Cyanides

We report the preparation, through palladium-catalyzed transformations, of the indolylfulgimide linker conjugate **1**, containing an adamantane core and nitrile anchoring groups. The ethynylene-linker **12** for the final Sonogashira coupling was prepared through palladium-mediated cyanation of an iodo-substituted precursor with $Zn(CN)_2$. The synthesis of the 6-bromo-substituted indolylfulgimide coupling partner **2** was accomplished in seven steps. Model studies using phenylacetylene and the 5-bromo-substituted indole **13** were conducted to find conditions that would prevent homocoupling of the ethynylene linker **12** in the final Sonogashira coupling step. The use of $Pd(PhCN)_2Cl_2$ and $[(tBu)_3PH]BF_4$ in the presence of diisopropylamine, together with CuI as additive, proved to be most efficient. Finally, the photochromic properties of conjugate **1** and indolylfulgimide **2** were studied.

Introduction

The rapid development of novel technologies in opto- and bioelectronics has produced strong interest in novel functional materials.[1] Photoswitchable organic molecules are promising candidates in these areas of interest. A detailed understanding of the elementary switching processes on surfaces is of fundamental importance for the development of photoswitches for nano- and optoelectronic devices,[2] and these processes strongly depend upon the assembling of the functional molecules on metals or semiconductors. Recently, rigid tripodal linker systems with multiple anchoring groups for the immobilization of chromophores have been developed by Galoppini and others.[3] These linker scaffolds offer new opportunities to vary the orientations of chromophore units and to influence their lateral interactions in ensembles or monolayers on surfaces. In continuation of our efforts directed towards the synthesis of photoswitch linker conjugates[4] we present here the synthesis of the indolylfulgimide linker conjugate **1**, containing an adamantane core at the center of the tetrahedral linker scaffold and nitrile anchoring groups for immobilization on metal surfaces (Figure 1). In the past, mainly thiol-based strategies have been applied for metal–molecule contacts on gold, silver, and copper. However, it has been shown that nitrile groups can also be used.[5]



(*E*/*Z*)-**1**

Figure 1. Structure of the fulgimide linker conjugate **1** (represented as a mixture of *E* and *Z* isomers).

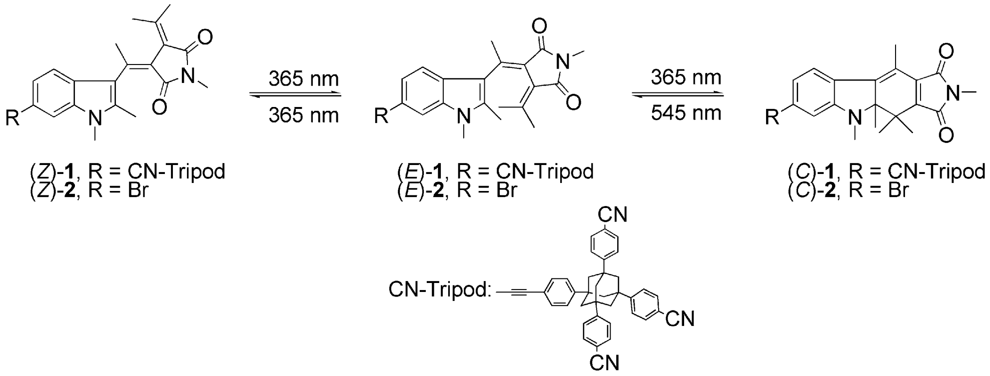
For applications in optoelectronics, photochromic compounds have to fulfil certain requirements, such as thermal stability of their photoisomeric states, potential for their individual states to be addressed specifically, and nondestructive read-out.[1] Fulgides and fulgimides show photochemical transitions between the ring-opened and the ring-closed states at appropriate wavelengths, together with high photochemical stabilities during repeated cycles of irradiation.[6] The photochromism and the photophysical characteristics of indolylfulgimide **2** (Scheme 1) in solution has already been characterized by Braun, Zinth, and ourselves.[7]

Fulgimides have also been identified as highly thermally and hydrolytically stable photochromic compounds.[8] Furthermore, the imide moiety can be used for the attachment of fluorophores.[9] Fulgimides and their parent fulgides each contain a hexa-1,3,5-triene structural element, and can exist in three isomeric forms: the noncyclizable *Z* form, the cyclizable *E* form, and the closed *C* form, which is obtained upon photochemical 6π-electrocyclization. The *Z* and *E* forms have similar optical properties and can be converted into each other by irradiation with UV light.

---

[a] Institut für Organische Chemie, Technische Universität Berlin,
Straße des 17. Juni 135, Sekr. C3, 10623 Berlin, Germany
Fax: +49-30-314-286-25
E-mail: krueck@chem.tu-berlin.de

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.



Scheme 1. Photochemical isomerization of the photoswitch linker conjugate **1** and the indolylfulgimide **2**.

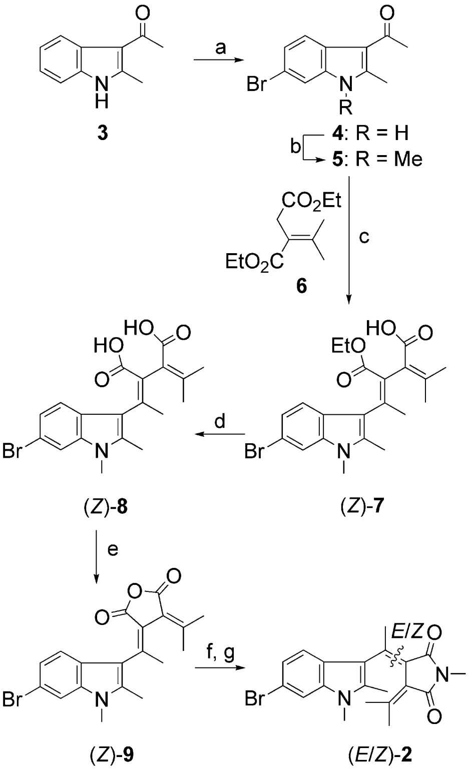
Only the *E* form undergoes the electrocyclic ring-closure reaction upon irradiation with UV light, which results in the formation of an almost planar cyclic *C* form (Scheme 1). The *E* form can be obtained by ring-opening of the *C* form upon irradiation with white light.

Results and Discussion

The bromo-substituted indolylfulgimide **2** was synthesized in seven steps starting from 3-acetyl-2-methyl indole (**3**) in 10% overall yield (Scheme 2). Treatment of indole **3** with bromine in glacial acetic acid afforded compound **4** in 68% yield. *N*-Methylation was accomplished with dimethyl carbonate (DMC), affording indole **5** in 78% yield after workup and recrystallization.

The bottleneck of all fulgide syntheses is usually the Stobbe condensation, for which potassium *tert*-butoxide and LDA are commonly used as bases.[8,10] However, with these bases the reaction between indole **5** and diethyl isopropylidenesuccinate (**6**) proceeded sluggishly, and the half-ester (*Z*)-**7** was isolated in poor yields. Fortunately, however, with potassium hexamethyldisilazide (KHMDS) in THF the half-ester (*Z*)-**7** was obtained in 36% isolated yield. The diacid was prepared next, by a two-step protocol. Firstly, the half-ester (*Z*)-**7** was treated with potassium *tert*-butoxide/*t*BuOH, and subsequently saponification was carried out with hot aqueous ethanolic KOH to give diacid (*Z*)-**8** in 86% yield. Anhydride formation by treatment with *N*-ethyl-*N′*-[3-(dimethylamino)propyl]carbodiimide (EDC) afforded the fulgide **9** in 91% yield as a 93:7 mixture of the *Z* and *E* isomers.

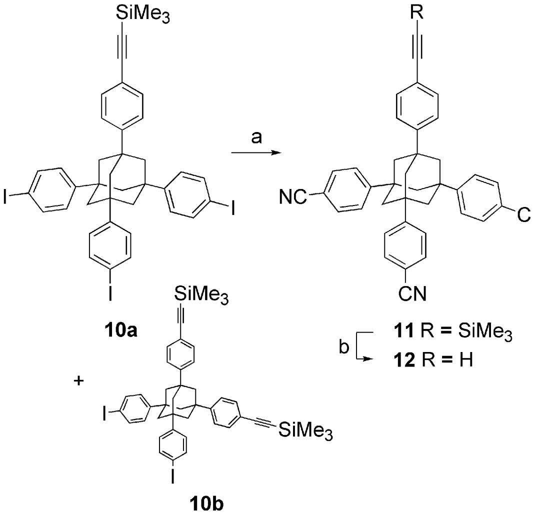
On treatment of fulgide **9** with methylamine hydrochloride in dioxane/water at room temperature in the presence of $NaHCO_3$ the regioisomeric succinamic acids were obtained as an inseparable mixture. This crude product mixture was used in the next step without purification. Treatment with 1 equiv. of $ZnCl_2$ and $ZnBr_2$ in the presence of HMDS (1.5 equiv.) in benzene at reflux gave fulgimide **2** (Scheme 2) in 67% yield over the two steps after workup and purification by flash chromatography as a 64:36 mixture of the *E* and *Z* isomers.[8] The pure *C* isomer (*C*)-**2** (Scheme 1) was obtained in 54% yield by irradiation of a solution of a *Z*/*E* isomeric mixture at 365 nm (200 W HBO) in DCM for 12 h and purification by flash chromatography. The *C* isomer (*C*)-**2**, dissolved in DCM, was then irradiated for 4 h with 545 nm light (1000 W, XBO) to yield the pure *E* isomer (*E*)-**2** (Scheme 1), quantitatively.



Scheme 2. Reagents and conditions: a) Br_2, AcOH, room temp., 72 h, **4**: 68%; b) DMC, K_2CO_3, DMF, reflux, 5 h, **5**: 78%; c) diethyl isopropylidenesuccinate (**6**), KHMDS, THF, 0 °C → room temp., 24 h, **7**: 36%; d) 1. KO*t*Bu/*t*BuOH, 80 °C, 2 h; 2. KOH/EtOH/H_2O, reflux, 2 h, **8**: 86%; e) EDC, DCM, room temp., 18 h, **9**: 91%; f) $MeNH_2$·HCl, $NaHCO_3$, dioxane/H_2O (4:1), room temp., 5 h, then g) $ZnCl_2$/$ZnBr_2$, HMDS, benzene, 60 °C, 19 h, **2**: 67%.

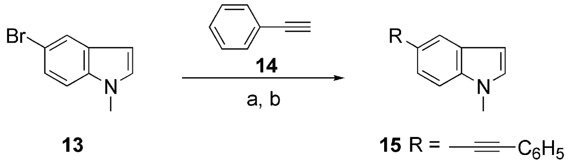
The synthesis of adamantane building block **12** was accomplished by starting with the known Sonogashira coupling between 1,3,5,7-tetrakis(4-iodophenyl)adamantane and (trimethylsilyl)acetylene,[3a] furnishing a mixture of the tri- and diiodo-substituted compounds **10a** and **10b**. This crude product mixture was used in the next step because of a more convenient chromatographic separation after the cyanation reaction.

For the introduction of the cyano anchoring groups, several methods were investigated. Classical methods for the conversion of aryl iodides into aryl nitriles, such as the Rosenmund–von Braun reaction, generally require harsh reaction conditions (150–250 °C) and are only suitable for robust substrates. A useful alternative is represented by palladium-mediated reactions in the presence of an excess of alkali or heavy metal cyanides,[11] which proceed at significantly lower temperatures. In a first approach we used potassium hexacyanoferrate(II) as a nontoxic cyanation agent and $Pd(OAc)_2$ in the presence of dppf and Na_2CO_3 in *N,N*-dimethylacetamide in a published procedure.[12] Unfortunately, the harsh reaction conditions (140 °C) led to decomposition of the starting material, so we attempted a milder Pd-mediated cyanation protocol with zinc cyanide.[13] Treatment of iodoadamantanes **10a** and **10b** with zinc cyanide in the presence of $Pd(dmdba)_2$, $[(tBu)_3PH]BF_4$, and zinc dust in NMP at room temperature for 24 h gave the corresponding nitrile **11** in 66% yield after workup and flash chromatography. Fortunately, compound **11** was also obtained in 80% yield on use of $Pd(PPh_3)_4$ and zinc cyanide in DMF at 65 °C for 28 h (Scheme 3); smaller amounts of by-products were formed during this procedure. Subsequent removal of the trimethylsilyl group with tetrabutylammonium fluoride (TBAF) afforded nitrile **12** in 91% yield (Scheme 3).



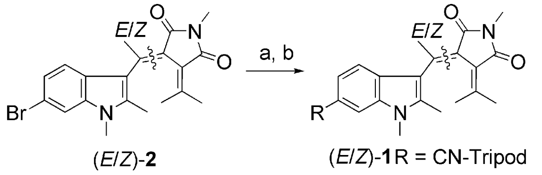
Scheme 3. Reagents and conditions: a) $Pd(PPh_3)_4$, $Zn(CN)_2$, DMF, 65 °C, 28 h, **11**: 80%; b) TBAF, THF, room temp., 12 h, **12**: 91%.

The key reaction in the synthesis of the photoswitch linker conjugate **1** is a palladium-mediated Sonogashira coupling of the electron-rich and deactivated 6-bromoindolyl fulgimide **2** with the tripodal linker **12**. To find the optimum reaction conditions for the Sonogashira coupling, model studies were carried out. Only a few examples of comparable palladium-mediated coupling reactions with halogenated indoles are known in the literature,[14] and no differences in the reactivities of 5- and 6-substituted halogenated indoles were detected in these studies,. We therefore selected the easily accessible 5-bromo-1-methyl-1*H*-indole (**13**) and phenylacetylene (**14**) as model compounds (Scheme 4). Under standard Sonogashira conditions[4] [$Pd(PPh_3)_2Cl_2$ (5%), CuI (10%), and triethylamine (30 equiv.) in THF at 60 °C], product **15** could not be detected, and only the homocoupled dimer of phenylacetylene (**14**) was obtained. Such Glaser-type side reactions often occur during the application of copper salts in Sonogashira reactions at higher temperatures.[15] Next, to take advantage of the higher reactivities of aryl iodides in cross-coupling reactions, coupling procedures including the exchange of bromine for iodine prior to the cross-coupling were examined. Treatment of indole **13** in a one-pot procedure with KI and 1,10-phenanthroline monohydrate in the presence of CuI at 110 °C, followed by standard Sonogashira conditions (Scheme 4), furnished indole **15** in 59% yield after workup and flash chromatography.



Scheme 4. Reagents and conditions: a) 1,10-phenanthroline monohydrate, CuI, KI, DMF, 110 °C, 48 h; b) 5% $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, DMF, room temp., 19 h, **15**: 59%.

Analogously, the indolylfulgimide **2** was treated with the tripodal linker **12** to yield the photoswitch linker conjugate **1** in 29% yield (17 µmol scale, *E*/*Z* = 79:21, Scheme 5). However, by-product formation and a low reproducibility, probably as a result of the harsh reaction conditions needed for the bromine–iodine exchange and incomplete conversion to the aryl iodide, forced us to examine other reaction conditions.



Scheme 5. Reagents and conditions: a) 1,10-phenanthroline monohydrate, CuI, KI, 110 °C, 36 h, DMF; b) **12**, 5% $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, DMF, room temp. 18 h, **1**: 29%.

Model compound **13** was thus once more examined, this time under alternative copper-free Sonogashira conditions directed towards prevention of the formation of the homocoupled dimer discussed above (Table 1).

With $Pd(PPh_3)_4$ as a catalyst in pyrrolidine at 50 °C, indole **15** was obtained in 65% yield (Table 1, Entry 1). However, in diisopropylethylamine under otherwise identical reaction conditions no conversion of the starting material was detected (Table 1, Entry 2). Therefore, as an additional alternative, some novel, highly reactive ligand systems were also explored. Fu and Buchwald have demonstrated that $Pd(PhCN)_2Cl_2$ in combination with the strongly basic and

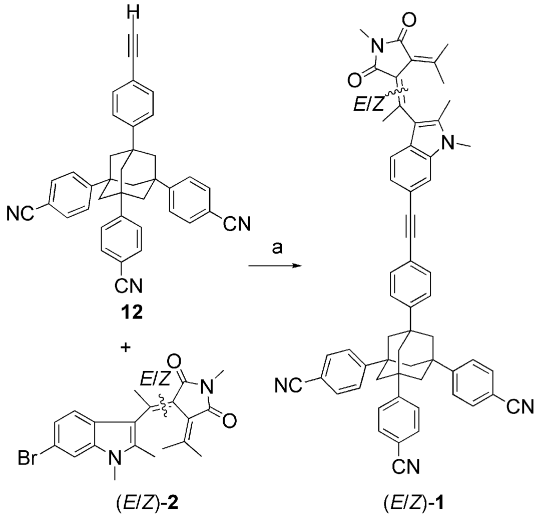
Table 1. Optimization of the Sonogashira coupling reaction between indole **13** and phenylacetylene (**14**) to furnish product **15**.

Entry	Reaction conditions	Time [h]	% Yield[a]
1	$Pd(PPh_3)_4$ (5%), pyrrolidine, 50 °C	40	65
2	$Pd(PPh_3)_4$ (5%), DIEA, 50 °C	24	–
3	$Pd(PhCN)_2Cl_2$ (3%), CuI (2%), $[(t\text{Bu})_3PH]BF_4$ (6%), room temp., DIPA, dioxane	18	94

[a] Isolated yield.

bulky tri-*tert*-butylphosphane serves as a versatile catalyst system for Sonogashira reactions with a broad range of differently substituted aryl bromides at room temperature.[16] Fortunately, the air-sensitive tri-*tert*-butylphosphane can be replaced by the stable tetrafluoroborate salt $[(t\text{Bu})_3PH]BF_4$ in the presence of a base.[17]

The indole **13** and phenylacetylene (**14**) were thus treated with $Pd(PhCN)_2Cl_2$ and $[(t\text{Bu})_3PH]BF_4$, in the presence of CuI (2%) and diisopropylamine (1.2 equiv.) at room temperature in dioxane, to afford product **15** in 94% yield (Table 1, Entry 3). Encouraged by these results, we employed similar reaction conditions for the reaction between indolylfulgimide **2** and the tripodal linker **12**, with the exception that CuI (4%) was used. The indolyl linker conjugate **1** was isolated in a reproducible 36% yield (41 µmol scale, *E*/*Z* 74:26, Scheme 6) after workup and purification by flash chromatography.



Scheme 6. Preparation of photoswitch linker conjugate **1**. Reagents and conditions: a) $Pd(PhCN)_2Cl_2$ (3%), $[(t\text{Bu})_3PH]BF_4$, CuI (4%), DIPA, dioxane, room temp., 20 h, **1**: 36%.

The photochromic behavior of compounds **1** and **2** was investigated in benzene solution at room temperature (Figure 2). The absorption spectra of the mixture of the open isomers of the photoswitch linker conjugate **1** showed two significant bands at 318 and 341 nm. The maximum of the open forms of the bromo-substituted indolylfulgimide **2** appeared at 354 nm. A dominant influence of the linker system in the region below 360 nm causes a significantly higher absorption in this region, thereby complicating comparison of the absorption spectra of compounds **1** and **2**. The open forms were then converted into the closed indolylfulgimides by irradiation with 365 nm light. For the photoswitch linker conjugate **1** the pericyclic ring closure is accompanied by an increasing absorption band at 567 nm, which is red-shifted by about 16 nm in relation to indolylfulgimide **2**. Furthermore, decreases in the peaks at 318 nm (compound **1**) and 354 nm (compound **2**) are seen. Because of the *Z*-to-*E* isomerization prior to cyclization, isosbestic points for this electrocyclic ring-closure process are not observed. The opposite ring-opening reactions to the *E* isomers occur on irradiation with green light and are indicated by complete disappearance of the bands at 567 nm (compound **1**) or 551 nm (compound **2**).

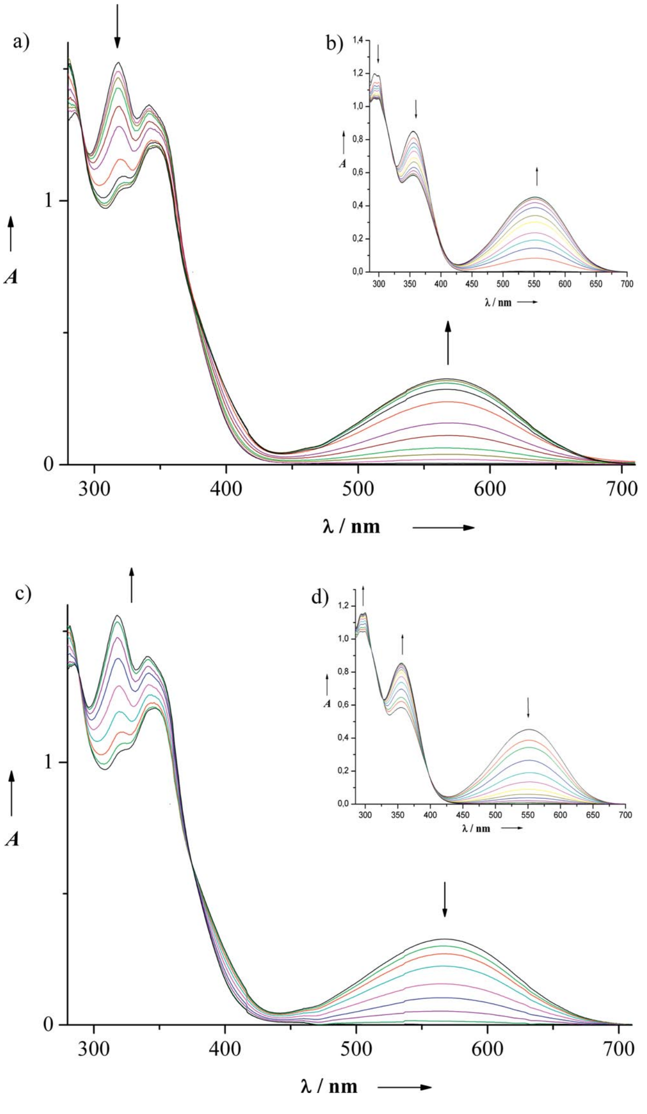


Figure 2. Top: ring-closure activated by irradiation at 365 nm (200 W, HBO). a) Conjugate **1** (c = 5.06×10^{-5} mol L^{-1}): after 0 s, 1 s, 2 s, 6 s, 10 s, 18 s, 40 s, 80 s, 120 s, 3 min, 15 min; b) fulgimide **2** (c = 1.05×10^{-4} mol L^{-1}): after 0 s, 2 s, 5 s, 8 s, 10 s, 15 s, 20 s, 30 s, 40 s, 60 s, 90 s, 120 s, 180 s. Bottom: Ring-opening reaction activated by irradiation at 545 nm (1000 W, XBO). c) Conjugate **1**: after 0 s, 1 s, 2 s, 4 s, 8 s, 14 s, 22 s, 36 s, 90 s, and d) fulgimide **2**: after 0 s, 2 s, 4 s, 6 s, 8 s, 10 s, 12 s, 15 s, 20 s, 30 s, 45 s, 60 s, 90 s; for further details see the Supporting Information.

Two isosbestic points (Table 2) reveal a clean conversion of the *C* into the *E* isomers. The complete spectroscopic data for both compounds are listed in Table 2.

Table 2. Spectroscopic data for the fulgimides **1** and **2**.

	$\lambda_{\max,Z/E}$[a], (ε)[b]	$\lambda_{\max,C}$[a], (ε)[b]	Isosbestic points[a]
1	318, (29430)	346, (22453), 567, (11422)	289, 375
2	354, (7745)	551, (7211)	321, 396

[a] [nm]. [b] [$\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$].

The ratios of the isomers in the photostationary states (pss) at 365 nm were examined by RP-HPLC. For the photoswitch linker conjugate **1** a *Z*/*E*/*C* ratio of 23.3:22.5:54.2 was determined in the pss, and similar results were obtained for the indolylfulgimide **2** (*Z*/*E*/*C* = 26.9:19.8:53.3).

Conclusions

The indolylfulgimide linker conjugate **1** has been synthesized from the 6-bromo-substituted indolylfulgimide **2** and the ethynylene linker **12** by Sonogashira cross-coupling. The key intermediate in the synthesis of fulgimide **2** is the bromo-substituted indolylfulgide **9**, which was synthesized by use of KHMDS in the Stobbe condensation and EDC for the anhydride formation. For the synthesis of the ethynylene linker a practical palladium-catalyzed cyanation procedure with zinc cyanide was successfully applied. For the Sonogashira coupling, model studies with the 5-bromo-substituted indole **13** and phenylacetylene (**14**) were investigated, and a procedure using $\mathrm{Pd(PhCN)_2Cl_2}$ and tri-*tert*-butylphosphonium tetrafluoroborate in the presence of diisopropylamine as the catalyst system with CuI as additive at room temperature proved to be most efficient for preventing homo-coupling of the ethynylene-linker **12**. The UV/Vis data and photochromic properties of conjugate **1** and indolylfulgimide **2** in benzene have been determined and discussed.

Experimental Section

General: Solvents were used in p.a. quality and were dried by standard procedures prior to use. NMP and DMF were purchased anhydrous from Fluka and were used without further purification. The following compounds were prepared by literature procedures: 3-acetyl-2-methylindole (**3**), diethyl isopropylidenesuccinate (**6**) 1,3,5,7-tetraphenyladamantane, 1,3,5,7-tetrakis(4-iodophenyl)adamantane, and 3,5,7-tris(4-iodophenyl)-1-{4-[2-(trimethylsilyl)ethynyl]phenyl}adamantane (**10a**). All reactions were monitored by analytical thin-layer chromatography (TLC, silica gel, Merck 60 F254 plates). Melting points were measured with a Büchi melting point determination apparatus and are uncorrected. IR spectra were measured on a Nicolet Avatar 360 instrument as ATR (Attenuated Total Reflectance). The peaks are listed as wavenumbers ($\mathrm{cm^{-1}}$) and the peak intensities were abbreviated as follows: vs = very strong, s = strong, m = medium, w = weak, br = broad. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC 200 or AM 400 spectrometers. Solvents are mentioned for the particular substances. The residual solvent protons or carbons were used as internal standards, the chemical shifts are given in ppm relative to tetramethylsilane (TMS), and coupling constants are in Hz. MS and HRMS spectra were recorded on a Finnigan MAT 95 SQ instrument and the samples were ionized at an ionization potential of 70 eV. Elemental analyses were carried out by the Microanalytical Division of the Institute of Organic Chemistry at the University of Mainz (Germany) or were measured with an Elementar Vario EI instrument from Analytik Jena at the Institute of Chemistry, TU Berlin. UV/Vis spectra were measured on a Shimadzu UV-1601 UV/Vis spectrometer in the solvents stated (Uvasol quality) in 1 × 1 × 4 cm quartz cuvettes at 25 °C. A 1000-W Xe-lamp (XBO, Osram, Munich) in a lamp casing from Müller Elektronik was used for the irradiation experiments at 545 nm and a 200-W mercury short-arc lamp (HBO, Osram, Munich) for the experiments at 365 nm. Additionally, 25 mm interference filters (ø 25 mm; ± 2 nm) from Amko, an IR-filter (Müller Elektronik; MHO 60) and a lens were placed between lamp and probe.

X-ray Crystallographic Analysis of (*E*)-2: $\mathrm{C_{20}H_{21}BrN_2O_2}$ with M_r = 398.27 $\mathrm{g\,mol^{-1}}$; crystal size 0.16 × 0.26 × 0.32 mm; monoclinic crystal system with space group *C*2/*c* and *Z* = 8, *a* = 2105.98(10), *b* = 860.41(4), *c* = 2356.21(12) pm; *V* = 3.8344(3) $\mathrm{nm^3}$, $\rho_{\text{calcd.}}$ = 1.380 $\mathrm{Mg\,m^{-3}}$; *F*(000) = 1624; linear absorption coefficient μ = 2.158 $\mathrm{mm^{-1}}$; type of diffractometer: Siemens SMART CCD; *T* = 293(2) K; Mo-K_α radiation; θ range 1.90–25.00°; index ranges $-19 \le h \le 25$, $-9 \le k \le 10$, $-27 \le l \le 21$; reflections collected 11079; independent reflections 3326 (R_{int} = 0.1200); observed reflections 226 [$I > 2\sigma(I)$], reflection used for refinement 3326; program system used: SHELXS-97, SHELXL-97, and SHELXTL; empirical absorption correction, direct methods, full-matrix refinement at F^2 with all independent reflections, weighting scheme SHELXL; goodness-of-fit parameter (based on F^2) S = 0.927; residual densities $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ = 429 and 434 $\mathrm{e\,nm^{-3}}$. Hydrogen atoms: refined with riding model, refined with a temperature factor 1.5 times U_{eq} of the carbon atoms; non-hydrogen atoms: refined anisotropically. Data/restraints/parameters: 3326/0/226; *R* index (all data): wR_2 (based on F^2) = 0.2244; *R* index (conventional) [$I > 2\sigma(I)$]: R_1 (based on *F*) = 0.0775.[18]

3-Acetyl-6-bromo-2-methylindole (4): Bromine (33.9 g, 10.9 mL, 212 mmol) was added to a solution of 3-acetyl-2-methylindole (**3**, 18.4 g, 106 mmol) in glacial acetic acid (500 mL), and the resulting suspension was stirred at room temp. for 72 h (TLC monitoring). The reaction mixture was then poured into $\mathrm{Na_2S_2O_3}$ solution (0.1 M, 500 mL), and the precipitated crude product was filtered off and redissolved in ethyl acetate (800 mL). The organic phase was washed with concd. $\mathrm{NaHCO_3}$ solution (200 mL) and brine (200 mL) and dried ($\mathrm{MgSO_4}$). The solvent was removed in vacuo to give **4** as a yellow-white solid (18.2 g, 72.3 mmol, 68 %), which slowly turned red upon air contact. Compound **4** was used without further purification; m.p. 179–181 °C; R_f = 0.69 (pentane/ethyl acetate, 2:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 7.97 (d, ^3J = 8.6 Hz, 1 H), 7.54 (d, ^4J = 1.8 Hz, 1 H), 7.26 (dd, ^3J = 8.3, ^4J = 1.8 Hz, 1 H), 2.67 (s, 3 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 193.0, 145.0, 135.6, 126.0, 124.1, 122.3, 114.2, 113.7, 113.5, 30.8, 15.0 ppm. IR (ATR): $\tilde{\nu}$ = 3161 (m), 3121 (m), 3088 (m), 2991 (m), 2909 (m), 1613 (s), 1571 (m), 1451 (m), 1412 (m), 1201 (w), 969 (w), 913 (w), 810 (m) $\mathrm{cm^{-1}}$. MS (EI, 70 °C): *m*/*z* (%) = 251 (40) [M]$^+$, 236 (100). HRMS: calcd. for $\mathrm{C_{11}H_{10}BrNO}$ 250.9946; found 250.9950.

3-Acetyl-6-bromo-1,2-dimethylindole (5): Indole **4** (19.5 g, 77.4 mmol) was dissolved in DMF (400 mL). $\mathrm{K_2CO_3}$ (16.0 g, 116 mmol) and dimethyl carbonate (20.9 g, 232 mmol) were added, and the reaction mixture was heated at reflux for 5 h (TLC monitoring). The resulting solution was poured into water (1.93 L) and extracted with Et_2O (3 × 1.16 L). The organic layer was washed with aqueous HCl (1 M, 800 mL) and brine (800 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by recrystallization from MeCN to give **5** in 78% yield (16.1 g, 60.3 mmol) as a yellow solid, which was used without further purification; m.p. 103–105 °C. $R_f = 0.48$ (DCM). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.84$ (d, $^{3}J = 8.3$ Hz, 1 H), 7.45 (d, $^{4}J = 2.0$ Hz, 1 H), 7.33 (dd, $^{3}J = 8.3$, $^{4}J = 2.0$ Hz, 1 H), 3.65 (s, 3 H), 2.74 (s, 3 H), 2.63 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta =$ 194.3, 145.6, 137.6, 125.3, 125.1, 122.1, 115.6, 114.4, 112.7, 31.7, 29.8, 12.8 ppm. IR (ATR): $\tilde{\nu} =$ 3068 (w), 3049 (w), 2941 (w), 2923 (w), 1637 (s), 1515 (s), 1471 (s), 1402 (s), 1213 (m), 1152 (m), 1032 (m), 935 (m), 804 (m), 746 (m) cm^{-1}. MS (EI, 100 °C): m/z (%) = 265 (40) $[M]^+$, 250 (100), 187 (25), 172 (70), 143 (20), 115 (20). HRMS: calcd. for $C_{12}H_{12}BrNO$ 265.0102; found 265.0103. $C_{12}H_{12}BrNO$ (266.13): C 54.16, H 4.54, N 5.26; found C 54.18, H 4.58, N 5.27.

4-(6-Bromo-1,2-dimethyl-1*H*-indol-3-yl)-3-(ethoxycarbonyl)-2-(propan-2-ylidene)pent-3-enoic Acid (7): Hexamethyldisilazane potassium salt (KHMDS, 4.20 g, 21.0 mmol) was dissolved in THF (250 mL) and the solution was cooled to 0 °C. A solution of diethyl isopropylidenesuccinate (**6**) (4.67 g, 21.8 mmol) in THF (40 mL) was added, and the resulting orange-yellow reaction mixture was stirred for 30 min at 0 °C. A solution of **5** (4.00 g, 15.0 mmol) in THF (40 mL) was then added over 30 min at 0 °C. The reaction mixture was allowed slowly to reach room temp. and stirred for 18 h (TLC monitoring). Aqueous HCl (2 M, 250 mL) was then added and the reaction mixture was extracted with Et_2O (4 × 125 mL). The combined organic layers were washed with brine (125 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by recrystallization from MeCN to give (*Z*)-**7** in 36% yield [2.33 g, 5.38 mmol, $Z/E \geq 95:5$ by ^{1}H NMR] as a yellow solid. ***Z* isomer**: M.p. 173–175 °C. $R_f = 0.27$ (DCM/MeCN, 10:1) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.39$ (d, $^{3}J = 1.6$ Hz, 1 H), 7.25 (d, $^{3}J = 8.4$ Hz, 1 H), 7.15 (dd, $^{3}J = 8.4$, $^{4}J = 1.7$ Hz, 1 H), 3.93–3.76 (m, 2 H), 3.63 (s, 3 H), 2.30 (s, 3 H), 2.26 (s, 3 H), 2.06 (s, 3 H), 1.97 (s, 3 H), 0.73 (t, $^{3}J = 7.1$ Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta =$ 170.5, 169.4, 151.9, 143.8, 137.6, 133.7, 129.5, 125.7, 125.1, 122.7, 120.0, 114.6, 114.5, 111.9, 60.8, 29.8, 24.0, 22.8, 22.5, 13.7, 11.3 ppm. IR (ATR): $\tilde{\nu} =$ 3064 (m), 2979 (m), 2936 (m), 1687 (s), 1619 (m), 1551 (w), 1515 (w), 1474 (s), 1405 (m), 1231 (s), 1207 (s), 1178 (s), 1054 (m), 966 (m), 902 (m), 865 (w), 802 (m), 748 (w) cm^{-1}. MS (EI, 240 °C): m/z (%) = 435 (100) $[M + H]^+$, 418 (76), 388 (12), 344 (24), 249 (20), 223 (40), 204 (30), 194 (24), 168 (16). HRMS: calcd. for $C_{21}H_{24}BrNO_4$ 433.0889; found 433.0888. $C_{21}H_{24}BrNO_4$ (434.32): C 58.07, H 5.57, N 3.22; found C 58.43, H 5.57, N 3.35.

2-[1-(6-Bromo-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-3-isopropylidenesuccinic Acid (8): Solid potassium *tert*-butoxide (7.43 g, 66.2 mmol) was added to a solution of (*Z*)-**7** (5.75 g, 13.2 mmol) in *tert*-butanol (150 mL). The mixture was stirred at 80 °C for 2 h (TLC monitoring). The solvent was then removed in vacuo and the residue was redissolved in ethanol (50 mL). A solution of potassium hydroxide (186 g, 331 mmol) in water (50 mL) was added, and the mixture was heated at reflux for 2 h (TLC monitoring). The reaction mixture was then poured into aqueous HCl (2 M)/ice (200 mL). The aqueous layer was saturated with neat NaCl and extracted with ethyl acetate (3 × 100 mL). The organic layer was washed with brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo to give the crude diacid (*Z*)-**8** (4.64 g, 11.4 mmol, 86%) as a brown solid, which was used without further purification, m.p. 203 °C. $R_f = 0.77$ (MeOH). ^{1}H NMR (400 MHz, $[D_6]$DMSO, 25 °C): $\delta = 7.64$ (d, $^{4}J = 1.6$ Hz, 1 H), 7.24 (d, $^{3}J = 8.4$ Hz, 1 H), 7.10 (dd, $^{3}J = 8.4$, $^{4}J = 1.6$ Hz, 1 H), 3.65 (s, 3 H), 2.27 (s, 3 H), 2.16 (s, 3 H), 1.92 (s, 3 H), 1.88 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $[D_6]$DMSO, 25 °C): $\delta =$ 168.3, 168.0, 147.4, 139.6, 137.2, 134.3, 131.1, 126.6, 125.3, 121.6, 119.9, 114.2, 113.0, 112.0, 29.6, 23.6, 22.5, 21.8, 11.0 ppm. IR (ATR): $\tilde{\nu} =$ 3056 (s), 2976 (s), 2943 (m), 1680 (s), 1623 (m), 1550 (w), 1475 (m), 1428 (m), 1405 (m), 1366 (m), 1330 (m), 1250 (s), 1212 (m), 1182 (m), 1086 (w), 1054 (w), 965 (m), 902 (m), 818 (m), 801 (m) cm^{-1}. MS (EI, 170 °C): m/z (%) = 405 (76) $[M]^+$, 390 (100), 250 (20), 222 (72), 204 (36). HRMS calcd. for $C_{19}H_{20}BrNO_4$, 405.0576; found 405.0575.

3-[1-(6-Bromo-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-4-(propan-2-ylidene)-3,4-dihydrofuran-2,5-dione (9): *N*-Ethyl-*N'*-[3-(dimethylamino)propyl]carbodiimide (EDC, 598 mg, 3.86 mmol) was added to a solution of (*Z*)-**8** (1.05 g, 2.58 mmol) in DCM (100 mL). The reaction mixture was stirred for 18 h at room temp. (TLC monitoring). The solution was then diluted with DCM (100 mL) and washed with aqueous HCl (0.1 M, 75 mL). The organic layer was washed with brine (75 mL), dried ($MgSO_4$), and concentrated in vacuo to give fulgide **9** in 91% yield (905 mg, 2.34 mmol, mixture of *Z*/*E* isomers 93:7, ^{1}H NMR); m.p. 196–198 °C (mixture). $R_f =$ 0.58 (DCM). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): ***Z* isomer**: $\delta =$ 7.46 (d, $^{4}J = 1.3$ Hz, 1 H), 7.40 (d, $^{3}J = 8.5$ Hz, 1 H), 7.22 (dd, $^{3}J = 8.5$, $^{4}J = 1.4$ Hz, 1 H), 3.70 (s, 3 H), 2.46 (s, 3 H), 2.36 (s, 3 H), 2.35 (s, 3 H), 2.03 (s, 3 H) ppm. ***E* isomer**: $\delta =$ 3.65 (s, 3 H), 2.77 (s, 3 H), 2.20 (s, 3 H), 2.19 (s, 3 H), 0.94 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): ***Z* isomer**: $\delta =$ 164.0, 161.3, 152.3, 147.4, 141.4, 138.1, 125.0, 123.8, 122.1, 120.7, 120.2, 115.2, 112.7, 112.4, 30.3, 27.3, 24.9, 22.5, 12.3 ppm. ***E* isomer**: $\delta =$ 30.2, 26.4, 23.7, 22.9, 12.3 ppm. IR (ATR): $\tilde{\nu} =$ 3067 (w), 2927 (m), 2856 (m), 1805 (s), 1753 (s), 1589 (m), 1474 (m), 1440 (m), 1404 (m), 1227 (s), 1134 (m), 958 (m), 924 (s) cm^{-1}. MS (EI, 160 °C): m/z (%) = 387 (40) $[M]^+$, 344 (20), 316 (20), 224 (50), 143 (30), 56 (100). HRMS: calcd. for $C_{19}H_{18}BrNO_3$ 387.0470; found 387.0471. $C_{19}H_{18}BrNO_3$ (388.26): C 58.78, H 4.67, N 3.61; found, C 58.72, H 4.69, N 3.54.

3-[1-(6-Bromo-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-1-methyl-4-(propan-2-ylidene)pyrrolidine-2,5-dione (2): $NaHCO_3$ (648 mg, 7.72 mmol) and methylamine hydrochloride (521 mg, 7.72 mmol) were added to a solution of fulgide **9** (1.50 g, 3.86 mmol, *Z*/*E* mixture) in 1,4-dioxane (200 mL) and water (50 mL), and the solution was stirred for 5 h at room temp. (TLC monitoring). After addition of ethyl acetate (100 mL) the organic layer was separated and washed with aqueous HCl (1 M, 75 mL). The aqueous layer was extracted with ethyl acetate (100 mL) and the combined organic layers were washed with brine (75 mL), dried ($MgSO_4$), and concentrated in vacuo to give the crude product as a brown solid in 95% yield (1.53 g, 3.65 mmol); mixture of isomers, ratio I:II = 66:33, ^{1}H NMR spectroscopy.

For the following reaction step, the crude product (419 mg, 1.00 mmol) was dissolved in benzene (40 mL) and heated to 60 °C. At this temperature $ZnBr_2$ (225 mg, 1.00 mmol) and HMDS (240 mg, 1.50 mmol) were added, whereupon a voluminous precipitate was observed. $ZnCl_2$ (1.00 mmol, 1 M in Et_2O) was then added, and the precipitate partially redissolved. The reaction mixture was stirred for 19 h at 60 °C (TLC monitoring). Afterwards the mixture was allowed to cool to room temp. and DCM (100 mL) was added. The reaction solution was then washed with brine (75 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography on silica (DCM/MeCN, 100:1) to give **2** as a yellow solid in 67% yield (279 mg, 697 µmol, *E*/*Z* mixture of isomers 64:36, ^{1}H NMR) calculated over two steps. For X-ray analysis compound (*E*)-**2** could be separated by recrystallisation from DCM as yellow prisms; m.p. 75–80 °C (mixture). $R_f = 0.32$

(DCM/MeOH, 10:1). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): ***E* isomer**: δ = 7.42 (d, ^4J = 1.6 Hz, 1 H), 7.26 (d, ^3J = 8.4 Hz, 1 H), 7.21 (dd, ^3J = 8.4, ^4J = 1.6 Hz, 1 H), 3.63 (s, 3 H), 3.11 (s, 3 H), 2.74 (s, 3 H), 2.17 (s, 3 H), 2.13 (s, 3 H), 0.90 (s, 3 H) ppm. ***Z* isomer**: δ = 7.43 (d, ^4J = 1.6 Hz, 1 H), 7.35 (d, ^3J = 8.4 Hz, 1 H), 7.17 (dd, ^3J = 8.4, ^4J = 1.6 Hz, 1 H), 3.69 (s, 3 H), 2.92 (s, 3 H), 2.45 (s, 3 H), 2.34 (s, 3 H), 2.26 (s, 3 H), 1.99 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): ***E* isomer**: δ = 169.4, 168.9, 147.7, 142.5, 138.0, 134.9, 124.5, 124.0, 123.9, 123.5, 120.9, 117.4, 115.3, 112.3, 30.1, 26.2, 23.9, 22.8, 22.1, 12.1 ppm. ***Z* isomer**: δ = 169.0, 166.4, 146.5, 140.7, 139.5, 137.8, 125.3, 125.0, 124.7, 123.2, 120.5, 114.6, 112.6, 112.4, 30.2, 27.1, 25.0, 23.7, 21.7, 12.0 ppm. IR (ATR): $\tilde{\nu}$ = 3435 (w), 2970 (w), 2929 (w), 2867 (w), 1765 (w), 1753 (w), 1699 (s), 1592 (m), 1547 (m), 1436 (m), 1384 (m), 1277 (m), 1018 (w) cm^{-1}. MS (EI, 150 °C): *m*/*z* (%) = 402 (100) [M + 2H]$^+$, 358 (20), 330 (24), 300 (30), 265 (24), 250 (60), 223 (100), 84 (74). HRMS: calcd. for $C_{20}H_{21}BrN_2O_2$ 400.0787; found 400.0787. $C_{20}H_{21}BrN_2O_2$ (400.08), C 59.86, H 5.27, N 6.98; found, C 59.82, H 5.29, N 6.79.

(*C*)-3-[1-(6-Bromo-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-1-methyl-4-(propan-2-ylidene)pyrrolidine-2,5-dione [(*C*)-2]: A solution of **2** (*E*/*Z* mixture, 120 mg, 0.33 mmol) in DCM (80 mL) was irradiated in a 100 mL round-bottomed flask for 12 h with a high-pressure mercury lamp (200 W HBO) and a 365 nm interference filter. The deep blue solution was then concentrated in vacuo. The isomers were separated in the dark by flash chromatography on silica gel with DCM as eluent to give the *C* isomer (65 mg, 0.16 mmol, 54%) as a deep blue solid, together with an *E*/*Z* mixture [*E*/*Z* = 72:28 (^{1}H NMR), 55 mg, 0.14 mmol, 46%] as a yellow solid. ***C* isomer**: M.p. 136–138 °C; R_f 0.46 (DCM/MeCN, 100:1). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 7.35 (d, ^3J = 8.2 Hz, 1 H), 6.81 (dd, ^3J = 8.2, ^4J = 1.7 Hz, 1 H), 6.64 (d, ^4J = 1.7 Hz, 1 H), 2.96 (s, 3 H), 2.86 (s, 3 H), 2.36 (s, 3 H), 1.74 (s, 3 H), 1.24 (s, 3 H), 1.13 (s, 3 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$, 25 °C): δ = 170.3, 169.5, 157.7, 148.2, 137.9, 136.9, 126.6, 125.8, 123.7, 120.9, 115.9, 111.0, 73.3, 40.0, 31.7, 23.5, 20.0, 18.9, 15.7, 13.8 ppm. IR (ATR): $\tilde{\nu}$ = 3418 (w), 2982 (w), 2938 (w), 1742 (m), 1690 (s), 1601 (w), 1425 (m), 1369 (m), 1267 (w), 1019 (w) cm^{-1}. MS (EI, 130 °C): *m*/*z* (%) = 400 (84) [M]$^+$, 385 (20), 328 (24), 300 (28), 248 (20), 223 (100). HR-MS: calcd. for $C_{20}H_{21}BrN_2O_2$ 400.0787; found 400.0784.

(*E*)-3-[1-(6-Bromo-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-1-methyl-4-(propan-2-ylidene)pyrrolidine-2,5-dione [(*E*)-2]: A solution of (*C*)-**2** (50 mg, 125 µmol) in DCM (80 mL) was irradiated in a 100 mL round-bottomed flask for 4 h with a xenon lamp (1000 W, XBO) and a 545 nm interference filter. The solvent was then removed in vacuo to give the *E* isomer quantitatively as a pale yellow solid (50 mg, 125 µmol). ***E* isomer**: M.p. 143–147 °C. R_f = 0.32 (DCM/MeOH, 10:1). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.42 (d, ^4J = 1.6 Hz, 1 H), 7.25 (d, ^3J = 8.4 Hz, 1 H), 7.19 (dd, ^3J = 8.4, ^4J = 1.6 Hz, 1 H), 3.62 (s, 3 H), 3.10 (s, 3 H), 2.74 (s, 3 H), 2.16 (s, 3 H), 2.13 (s, 3 H), 0.89 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 169.3, 168.9, 147.7, 142.4, 138.0, 134.9, 124.4, 123.9, 123.8, 123.5, 120.9, 117.3, 115.2, 112.2, 30.0, 26.2, 23.8, 22.7, 22.0, 12.1 ppm. IR (ATR): $\tilde{\nu}$ = 3509 (w), 2970 (w), 2938 (w), 2907 (w), 1742 (m), 1689 (m), 1601 (w), 1473 (w), 1427 (m), 1369 (m), 1270 (m), 1018 (m) cm^{-1}. MS (EI, 165 °C): *m*/*z* (%) = 400 (90) [M]$^+$, 328 (28), 300 (30), 223 (100). HR-MS: calcd. for $C_{20}H_{21}BrN_2O_2$ 400.0787; found 400.0788.

4,4′,4′′-(7-{4-[2-(Trimethylsilyl)ethynyl]phenyl}adamantane-1,3,5-triyl)tribenzonitrile (11): A nitrogen-purged reaction tube was loaded with a crude mixture of 3,5,7-tris(4-iodophenyl)-1-{4-[2-(trimethylsilyl)ethynyl]phenyl}adamantane (**10a**) and 5,7-bis(4-iodophenyl)-1,3-bis{4-[2-(trimethylsilyl)ethynyl]phenyl}adamantane (**10b**); (750 mg, **10a**/**10b** = 1:3), Pd(PPh$_3$)$_4$ (94.8 mg, 82.0 µmol), and zinc cyanide (289 mg, 2.46 mmol). The reaction tube was evacuated and refilled with nitrogen (3×), and DMF (1 mL) was then added. The yellow suspension was stirred for 28 h at 65 °C, diluted with ethyl acetate (40 mL), filtered, and washed with water (3 × 50 mL) and brine (50 mL). The organic layer was dried (MgSO$_4$) and the solvents were evaporated to dryness. Purification by flash chromatography on silica (pentane/ethyl acetate, 8:1) gave pure **11** as a white solid (101 mg, 165 µmol, 80%); m.p. > 290 °C. R_f = 0.13 (pentane/ethyl acetate, 8:1). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.67 (d, ^3J = 8.6 Hz, 6 H), 7.57 (d, ^3J = 8.6 Hz, 6 H), 7.47 (d, ^3J = 8.4 Hz, 2 H), 7.37 (d, ^3J = 8.4 Hz, 2 H), 2.15 (s, 12 H), 0.25 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 153.5, 148.3, 132.6, 132.4, 126.0, 124.8, 121.8, 118.8, 110.7, 104.7, 94.6, 46.4, 46.4, 39.8, 39.3, 0.1 ppm. IR (ATR): $\tilde{\nu}$ = 3062 (w), 3041 (w), 2956 (m), 2931 (m), 2902 (m), 2854 (w), 2227 (s), 2157 (m), 1706 (w), 1607 (m), 1505 (s), 1448 (w), 1405 (m), 1361 (m), 1262 (w), 1249 (m), 1220 (w), 1175 (w), 1116 (w), 1018 (m), 865 (vs), 839 (vs), 804 (m), 792 (m), 760 (m), 700 (w) cm^{-1}. MS (EI, 300 °C): *m*/*z* (%) = 611 (41) [M]$^+$, 597 (48), 596 (100). HRMS: calcd. for $C_{42}H_{37}N_3Si$ 611.2756; found 611.2755.

4,4′,4′′-{7-[4-(Ethynyl)phenyl]adamantane-1,3,5-triyl}tribenzonitrile (12): TBAF (1 M in THF, 280 µmol) was added to a solution of nitrile **11** (70.0 mg, 114 µmol) in THF (9 mL). The solution was stirred for 12 h at room temp. After complete consumption of the starting material (TLC monitoring) the mixture was treated with water (15 mL) and extracted with DCM (3 × 20 mL). The organic layer was then dried (MgSO$_4$), and the solvents were evaporated to dryness. The crude product was purified by flash chromatography on silica (hexane/DCM, 1:1) to give **12** as a white solid (56.1 mg, 104 µmol, 91%); m.p. 293 °C. R_f = 0.24 (hexane/DCM, 1:1). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.66 (d, ^3J = 8.4 Hz, 6 H), 7.57 (d, ^3J = 8.4 Hz, 6 H), 7.50 (d, ^3J = 8.4 Hz, 2 H), 7.41 (d, ^3J = 8.4 Hz, 2 H), 3.07 (s, 1 H), 2.17–2.16 (m, 12 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 153.5, 148.7, 132.6, 132.5, 126.1, 125.0, 120.7, 118.9, 110.7, 83.3, 77.6, 46.4, 46.4, 39.8, 39.3 ppm. IR (ATR): $\tilde{\nu}$ = 3060 (w), 3032 (w), 2958 (m), 2931 (m), 2901 (m), 2855 (m), 2673 (w), 2549 (w), 2155 (w), 1686 (vs), 1608 (m), 1571 (w), 1504 (w), 1422 (m), 1358 (w), 1320 (w), 1287 (m), 1250 (m), 1190 (m), 1122 (w), 1109 (w), 1016 (m), 864 (m), 853 (m), 843 (m), 761 (m), 705 (w) cm^{-1}. MS (EI, 300 °C): *m*/*z* (%) = 539 (87) [M]$^+$, 515 (23), 436 (19), 382 (22), 368 (53), 281 (40), 210 (43), 116 (53), 97 (53), 83 (60), 69 (72), 57 (100). HRMS: calcd. for $C_{39}H_{29}N_3$ 539.2361; found 539.2369.

1-Methyl-6-(phenylethynyl)-1*H*-indole (15): A dried and nitrogen-purged reaction tube was loaded with 5-bromo-1-methyl-1*H*-indole (**13**, 200 mg, 952 µmol), Pd(PhCN)$_2$Cl$_2$ (10.9 mg, 28.6 µmol), (tri-*tert*-butylphosphonium)tetrafluoroborate (16.6 mg, 57.2 µmol), and copper(I) iodide (3.62 mg, 19.0 µmol) and was then evacuated and refilled with nitrogen (3×). Dioxane (4 mL), diisopropylamine (115 mg, 1.14 mmol), and phenylacetylene (**14**, 116 mg, 1.14 mmol) were then added by syringe, and the brown suspension was stirred for 18 h at room temp. After complete consumption of the starting material (TLC monitoring) the brown solution was diluted with ethyl acetate (50 mL) and filtered, and the solvents were evaporated to dryness. Purification by flash chromatography on silica (pentane/ethyl acetate, 40:1) gave **15** as a yellow solid (206 mg, 891 µmol, 94%); m.p. 118–120 °C. R_f = 0.29 (pentane/ethyl acetate, 40:1). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.86 (d, ^4J = 1.4 Hz, 1 H), 7.56 (dd, ^3J = 8.4, ^4J = 1.8 Hz, 2 H), 7.42 (dd, ^3J = 8.4, ^4J = 1.5 Hz, 1 H), 7.37–7.28 (m, 4 H), 7.08 (d, ^3J = 3.1 Hz, 1 H), 6.50 (dd, ^3J = 3.1, ^4J = 0.8 Hz, 1 H), 3.80 (s, 3 H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$, 25 °C): δ = 136.5, 131.6, 129.9, 128.5, 128.4, 127.8, 125.3, 125.0, 124.2, 113.9, 109.4, 101.5, 91.3, 87.2, 33.1 ppm. IR (ATR): $\tilde{\nu}$ = 3057 (w), 2928 (w), 2207 (w), 1596 (m), 1494 (s), 1443 (s), 1423 (w), 1364 (m), 1336 (w), 1273 (w), 1242 (w), 1153 (w), 1070 (w), 1029 (w), 914 (w), 884 (w), 830 (w), 802 (m), 755 (s), 720 (m), 691 (s) cm^{-1}. MS (EI, 160 °C): *m*/*z* (%) = 232 (18) $[M + H]^+$, 231 (100) $[M]^+$, 230 (17), 202 (7), 189 (6), 116 (9). HRMS: calcd. for $C_{17}H_{13}N$ 231.1048; found 231.1052.

4,4′,4′′-(7-{4-[(1,2-Dimethyl-3-{1-[1-methyl-2,5-dioxo-4-(propan-2-ylidene)pyrrolidin-3-ylidene]ethyl}-1*H*-indol-6-yl)ethynyl]phenyl}-adamantane-1,3,5-triyl)tribenzonitrile (1): A dried and nitrogen-purged reaction tube was loaded with an *E*/*Z* mixture of indolylfulgimide **2** (53.5 mg, 133 µmol), tripod **12** (60.0 mg, 111 µmol), $Pd(PhCN)_2Cl_2$ (1.27 mg, 3.33 µmol), (tri-*tert*-butylphosphonium) tetrafluoroborate (1.93 mg, 6.66 µmol), and copper(I) iodide (870 µg, 4.57 µmol) and was then evacuated and refilled with nitrogen (3 ×). Dioxane (1 mL) and diisopropylamine (13.4 mg, 133 µmol) were added by syringe, and the brown suspension was stirred for 20 h at room temp. The brown solution was diluted with ethyl acetate (30 mL) and filtered, and the solvents were evaporated to dryness. Purification by flash chromatography on silica (DCM/MeCN, 100:1) afforded **1** as a slightly green solid [35.0 mg, 40.7 µmol, 36%, *E*/*Z* mixture of isomers (74:26), ^1H NMR]; m.p. > 220 °C (decomposition). R_f = 0.09 (DCM/MeCN, 100:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): ***E* isomer**: δ = 7.67 (d, ^3J = 8.7 Hz, 6 H), 7.59–7.54 (m, 8 H), 7.48 (s, 1 H), 7.43 (d, ^3J = 8.6 Hz, 2 H), 7.35 (d, ^3J = 8.2 Hz, 1 H), 7.29–7.27 (m, 1 H), 3.68 (s, 3 H), 3.11 (s, 3 H), 2.77 (s, 3 H), 2.19–2.16 (m, 6 H *from fulgimide*, 12 H *from adamantane*), 0.90 (s, 3 H) ppm. ***Z* isomer**: δ = 3.73 (s, 3 H), 2.93 (s, 3 H), 2.46 (s, 3 H), 2.38 (s, 3 H), 2.30 (s, 3 H), 2.00 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): ***E* isomer**: δ = 169.4, 168.9, 153.6, 147.7, 147.7, 142.5, 136.8, 136.1, 132.6, 131.9, 126.0, 125.7, 125.0, 124.1, 123.9, 123.8, 122.4, 119.7, 118.8, 117.8, 115.8, 112.6, 110.8, 91.3, 87.9, 46.6, 46.5, 39.9, 39.3, 30.0, 26.1, 23.9, 22.9, 22.1, 12.2 ppm. ***Z* isomer**: δ = 30.2, 27.1, 25.0, 23.7, 21.7, 12.1 ppm. IR (ATR): $\tilde{\nu}$ = 3509 (w), 3060 (w), 2929 (m), 2853 (w), 2226 (s), 1741 (w), 1692 (vs), 1606 (s), 1506 (m), 1376 (m), 1364 (m), 1175 (m), 1018 (m), 835 (m), 793 (w), 753 (w) cm^{-1}. MS (EI, 300 °C): *m*/*z* (%) = 860 (12) $[M + H]^+$, 859 (19) $[M]^+$, 552 (15), 368 (20), 277 (43), 227 (80), 134 (62), 91 (100), 57 (59). HRMS: calcd. for $C_{59}H_{49}N_5O_2$ 859.3886; found 859.3869.

Supporting Information (see also the footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all synthesized compounds and spectroscopic data of compounds **1**, **2** and **9**.

Acknowledgments

This work was funded by the Volkswagen Foundation, the Deutsche Forschungsgemeinschaft (DFG) (SFB 658 and GK 352), and the Fonds der Chemischen Industrie.

---

[1] V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, **2003**.

[2] a) M. Alemani, M. V. Peters, S. Hecht, K.-H. Rieder, F. Moresco, L. Grill, *J. Am. Chem. Soc.* **2006**, *128*, 14446–14447; b) P. Dietrich, F. Michalik, R. Schmidt, C. Gahl, G. Mao, M. Breusing, M. Raschke, B. Priewisch, T. Elsässer, R. Mendelsohn, M. Weinelt, K. Rück-Braun, *Appl. Phys. A: Mater. Sci. Process.* **2008**, *93*, 285–292.

[3] a) E. Galoppini, W. Guo, W. Zhang, P. G. Hoertz, P. Qu, G. J. Meyer, *J. Am. Chem. Soc.* **2002**, *124*, 7801–7811; b) Y. Yao, J. M. Tour, *J. Org. Chem.* **1999**, *64*, 1968–1971; c) L. Wei, K. Padmaja, W. J. Youngblood, A. B. Lysenko, J. S. Lindsey, D. F. Bocian, *J. Org. Chem.* **2004**, *69*, 1461–1469.

[4] S. Zarwell, K. Rück-Braun, *Tetrahedron Lett.* **2008**, *49*, 4020–4025.

[5] U. Schlickum, R. Decker, F. Klappenberger, G. Zoppellaro, S. Klyatskaya, M. Ruben, I. Silanes, A. Arnau, K. Kern, H. Brune, J. V. Barth, *Nano Lett.* **2007**, *7*, 3813–3817.

[6] Y. Yokoyama, *Chem. Rev. (Washington,. DC,. U. S.)* **2000**, *100*, 1717–1739.

[7] a) B. Heinz, S. Malkmus, S. Laimgruber, S. Dietrich, C. Schulz, K. Rück-Braun, M. Braun, W. Zinth, P. Gilch, *J. Am. Chem. Soc.* **2007**, *129*, 8577–8584; b) S. Malkmus, F. O. Koller, B. Heinz, W. J. Schreier, T. E. Schrader, W. Zinth, C. Schulz, S. Dietrich, K. Rück-Braun, M. Braun, *Chem. Phys. Lett.* **2006**, *417*, 266–271; c) M. Braun, S. Malkmus, F. O. Koller, B. Heinz, W. Zinth, C. Schulz, S. Dietrich, K. Rück-Braun, *Springer Series in Chemical Physics* **2007**, *88*, 291–293.

[8] B. Otto, K. Rück-Braun, *Eur. J. Org. Chem.* **2003**, 2409–2417.

[9] S. D. Straight, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore, D. Gust, *Adv. Funct. Mater.* **2007**, *17*, 777–785.

[10] S. Uchida, Y. Yokoyama, J. Kiji, T. Okano, H. Kitamura, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2961–2967.

[11] M. Sundermeier, A. Zapf, M. Beller, *Eur. J. Inorg. Chem.* **2003**, 3513–3526.

[12] T. Schareina, A. Zapf, M. Beller, *Chem. Commun.* **2004**, 1388–1389.

[13] a) D. M. Tschaen, R. Desmond, A. O. King, M. C. Fortin, B. Pipik, S. King, T. R. Verhoeven, *Synth. Commun.* **1994**, *24*, 887–890; b) J. Ramnauth, N. Bhardwaj, P. Renton, S. Rakhit, S. P. Maddaford, *Synlett* **2003**, 2237–2239.

[14] K. Kumar, A. Zapf, D. Michalik, A. Tillack, T. Heinrich, H. Boettcher, M. Arlt, M. Beller, *Org. Lett.* **2004**, *6*, 7–10.

[15] D. Gelman, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2003**, *42*, 5993–5996.

[16] T. Hundertmark, A. F. Littke, S. L. Buchwald, G. C. Fu, *Org. Lett.* **2000**, *2*, 1729–1731.

[17] M. R. Netherton, G. C. Fu, *Org. Lett.* **2001**, *3*, 4295–4298.

[18] CCDC-711671 [for (*E*)-**2**] contains the supplementary crystallographic data for 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.

Received: December 2, 2008