Cross-Conjugation vs. Linear Conjugation in Donor–Bridge–Acceptor
Nitrophenol Chromophores

Mikkel Andreas Christensen,[a] Eduardo Antonio Della Pia,[a] Jørgen Houmøller,[b]
Steen Brøndsted Nielsen,[b] and Mogens Brøndsted Nielsen*[a]

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The influence of cross-conjugation vs. linear conjugation on the electronic communication between donor and acceptor groups in phenol(ate)–bridge–nitrobenzene chromophores was investigated by solution and gas-phase absorption spectroscopy, fluorescence spectroscopy, and quantum chemical calculations. The compounds studied include, among others, geminally and trans-substituted diethynylethenes prepared by stepwise Sonogashira cross-coupling reactions, and the cross-conjugated analogue of stilbene. A butadiyne-bridged donor–acceptor chromophore was prepared by an unsymmetrical Pd-catalysed coupling between a chloroalkyne and a terminal alkyne. While the linearly conjugated chromophores showed a strong and redshifted charge-transfer (CT) absorption maximum upon deprotonation in solution, a new redshifted absorption was either absent or present as a weak shoulder for the cross-conjugated derivatives. Calculations on the nonplanar 1,1-diaryl-substituted ethylene derivative revealed that the S0–S1 absorption has a very low oscillator strength due to insignificant coupling between the donor and acceptor ends. The energy of this CT absorption for a nonsolvated molecule is smaller than that of the linearly conjugated stilbene analogue by 0.4 eV. This result cannot directly be inferred from the solution studies. A gas-phase absorption spectrum of this chromophore was measured by action spectroscopy, which only revealed a higher-energy absorption band. Based on calculations, this band was assigned to a higher-lying π-π* transition. For the planar diethynylethene chromophores, cross-conjugation leads to a decrease of 0.3 eV in the excitation energy, according to the calculations. Finally, in contrast to the linearly conjugated chromophores, the cross-conjugated ones did not show any fluorescence, which may be due to deexcitation via the low-lying CT "dark" state.

Introduction

Organic molecules composed of donor and acceptor entities separated by a bridge usually show intramolecular charge-transfer (CT) transitions, and they are of interest as building blocks for advanced optical materials and photovoltaic devices, as well as in molecular electronics.[1] It is desirable to be able to fine-tune the position of the charge-transfer absorption for a specific donor–acceptor system by varying the electronic nature of the bridge between the two units. We have recently[2] studied a series of phenolate–bridge–nitrobenzene chromophores by both solution and gas-phase absorption spectroscopy, and the results revealed a clear trend: When the donor and acceptor units are weakly coupled via the connecting bridge, the CT absorption occurs at a lower energy. This result is also consistent with several studies on other donor–acceptor chromophores conducted, for example, by Diederich and co-workers.[3] In other words, inefficient conjugation between the two units leads to redshifted absorption maxima. This may at first seem counter to the usual perception of the influence of conjugation, and the fact that a longer linearly conjugated oligoene/oligoenyne absorbs at lower energy than a shorter one.[4] Indeed, extended conjugation at both ends of donor–acceptor chromophores plays a similar role by raising the HOMO energy of the donor and lowering the LUMO energy of the acceptor, thereby inducing a red-shift, but an additional mixing of these orbitals conveyed by the bridge should lead to the opposite effect. This is, for example, borne out by the fact that the absorption maximum of the weakly coupled m-nitrophenolate is redshifted relative to those of the o- and p-nitrophenolates, as shown by both solution and gas-phase studies.[2c–2d] In some cases,
however, solution studies can be misleading in terms of revealing the coupling between donor and acceptor units, due to solvation effects. Thus, from gas-phase absorption spectroscopy of O-/NO2 functionalized tolane and stilbene molecules, we have found that an alkyne bridge provides a less efficient coupling (redshifted absorption) than an alkene bridge, whereas the opposite and wrong conclusion would have been drawn from solution studies.[2b] Solution studies on tetrathiafulvalene–bridge–dicyanoethylene chromophores on the other hand support the less efficient coupling conveyed by an alkyne bridge.[5]

To shed further light on the tuning of the absorption of nitrophenolate(s), we decided to investigate the influence of cross-conjugation vs. linear conjugation. Several experimental and theoretical studies have revealed that cross-conjugation, as found for example in dendralenes,[6] results in less efficient π-electron delocalization than linear conjugation.[4,7] A too weak coupling between donor and acceptor units may lead to the disappearance of the CT transition in the electronic absorption spectrum or to a very weak band, which can complicate the interpretation of spectroscopic data. Indeed, the CT absorption of m-nitrophenolate is much weaker than those of o- and p-nitrophenolates.[2c]

Figure 1 shows the compounds of interest for this study. The cross-conjugated and linearly conjugated geminal- and trans-diethynylethenes 1 and E-2 have C2 units between the central ethylene and aryl groups, which should allow the molecules to be planar. The properties of these compounds were compared to those of the linearly conjugated butadiyne 3, the cross-conjugated and nonplanar alkene 4, and the linearly conjugated fluorene 5, in which the two aryl groups are forced into planarity. Protocols for the synthesis of 1–4 are presented, as well as a modified procedure for known[8] compound 5.

Results and Discussion

The synthesis of compound 1 is shown in Scheme 1. First, known vinyl triflate[9] was treated with p-nitrophenylacetylene (7) in a Sonogashira coupling[10] to give geminally substituted diethynylethene 8. Desilylation of this compound provided terminal alkyne 9. A direct Sonogashira coupling between this compound and 4-iodophenol was not successful in our hands. Instead, we treated 9 with known aryl iodide 10,[11] which, gratifyingly, furnished compound 11. Finally, the ester group was cleaved to give target molecule 1.

The syntheses of E-2 and 3 are shown in Scheme 2. Known terminal alkyne 12,[12] (readily prepared from 10, see Supporting Information) was treated with vinyl bromide E-13[13] under Sonogashira conditions to give diethynylethene E-14. Cleavage of the ester group then gave compound E-2. We have recently shown that chloroalkynes undergo cross-coupling reactions with terminal alkynes under Sonogashira conditions as readily as aryl iodides.[14] This knowledge was conveniently used in the first step towards 3. Thus, 12 was treated with chloroalkyne 15[15] under Sonogashira conditions to give butadiyne 16. Finally, the ester group was cleaved to give phenol derivative 3.

Acetylation of ketone 17[16] gave compound 18 (Scheme 3), which was then subjected to a Wittig reaction followed by hydrolysis of the ester group during aqueous work-up of the reaction mixture to give 1,1-diarylethylene 4. For unknown reasons, the related benzoate of 18 (with an OBz instead of the OAc functionality) showed no reactivity towards the phosphorus ylide, and only starting material was recovered in that case. An alternative strategy for the
preparation of 4 by demethylation of the corresponding methoxy derivative\cite{17} (using either BBr₃, HBr, or Me₃SiI) proved unsuccessful (other unidentified products were obtained). Single crystals of 4 were grown from diethyl ether/heptane and subjected to X-ray crystallographic analysis. The structure revealed that the two aryl rings are rotated out of coplanarity (Figure 2). Thus, the angle between the ethylene plane and aryl plane C₃–C₈ is 32.6°, and the angle between the ethylene plane and aryl plane C₉–C₁₄ is 48.7°. It is well known that 1,1-diaryl ketones and ethylenes adopt a propeller conformation to avoid the ortho-H,H clash.\cite{18}

Conversion of aniline derivative 19 into fluorene derivative 5 has been described previously.\cite{8} However, we used similar conditions\cite{19} to those used to obtain the related OH/NO₂ substituted terphenyl compound (Scheme 4).

**Solution-Phase UV/Vis Spectroscopy**

The UV/Vis absorption spectra in MeOH of neutral chromophores 1–5 are shown in Figure 3 top, while those of the corresponding sodium phenolates are shown in Figure 3 bottom. The absorption maxima are collected in Table 1. Diethynylethene E-2 was observed to undergo photoisomerization to its Z isomer, whose longest-wavelength CT absorption has a lower intensity, as deduced from the absorption spectrum of the resulting mixture of the two isomers in photostationary equilibrium (see Supporting Information). The longest-wavelength absorptions of linearly conjugated chromophores E-2, 3, and 5 become significantly redshifted upon generation of the corresponding phenolates, consistent with the assumed CT character of these absorptions. Deprotonation of cross-conjugated compound 1 results instead in a blueshift of the longest-wavelength absorption. This observation seems to indicate that the actual CT absorption corresponding to a HOMO–LUMO transition (S₀–S₁) is in fact absent from the spectrum. Generation of the phenolate of cross-conjugated compound 4 does result in a new redshifted absorption, which appears as a weak shoulder/tail around 375 nm. We note that in previous studies on 1-(4-cyanophenyl)-1-[4-(dimethylamino)phenyl]ethylenne and 1-(4-cyanophenyl)-1-(4-methoxyphenyl)ethylenne a band, assigned to a CT absorption, was also observed as a
shoulder absorption at the red edge of the strong absorption band in the spectrum.\textsuperscript{20} To shed more light on the absorptions of the phenolate of 4, and on the character of these absorptions, we decided to turn to gas-phase experiments and calculations (vide infra), thereby avoiding having to take into account complicated solvation and counterion effects for this negatively charged species.

Figure 3. UV/Vis absorption spectra of chromophores in MeOH (top, neutral chromophores) and in MeOH + 1% NaOMe (bottom, phenolates).

<table>
<thead>
<tr>
<th>Neutral Phenolate\textsuperscript{[a]}</th>
<th>λ\textsubscript{max} [nm] (ε [M\textsuperscript{-1}cm\textsuperscript{-1}])</th>
<th>Phenolate\textsuperscript{[a]}</th>
<th>λ\textsubscript{max} [nm] (ε [M\textsuperscript{-1}cm\textsuperscript{-1}])</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>262 (45300), 293 (63700), 308 (58300), 346 (27300)</td>
<td>272 (60800), 312 (60500), 336 (50800, sh)</td>
<td></td>
</tr>
<tr>
<td>E-2</td>
<td>320 (30300), 368 (44370)</td>
<td>315 (32800), 416 (34900)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>241 (15000), 273 (13900), 287 (16400), 303 (16400), 361 (15800)</td>
<td>252 (20700), 310 (23200), 418 (10900)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>229 (37100), 269 (48000), 327 (16000, sh)</td>
<td>293 (64600), 375 (4700, sh)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>244 (5100), 364 (8000)</td>
<td>268 (5400), 430 (8000)</td>
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</table>

\textsuperscript{[a]}Corresponding to sodium phenolate (obtained by 1% NaOMe).

**Gas-Phase Action Spectroscopy**

The intrinsic optical properties of the phenolate of 4 were studied in the gas phase by action spectroscopy using the ELectrostatic Ion Storage ring in Aarhus (ELISA).\textsuperscript{21} Briefly, the number of photoinduced neutral fragment products was measured as a function of the excitation wavelength, and this number was used as a measure of the absorption cross-section (more details in Experimental Section). Figure 4 (top) shows the yield of neutral products formed in the first 15 μs after photoexcitation as a function of excitation wavelength. This signal is labeled Prompt SED in the Figure. The signal is strongest at the lowest wavelength of 420 nm, and it decreases almost linearly to about 480 nm. There is a long tail at higher wavelengths that extends up to about 650 nm (this tail is more clearly revealed when corrections for laser power were not done, see Supporting Information). As the vertical electron-detachment energy is 2.86 eV (434 nm) (vide infra), both direct electron detachment and dissociation can contribute to the signal at the lowest wavelengths. After half a revolution and later times, the delayed formation of neutral products was sampled (Figure 4, bottom). This signal was recorded both with the SED and the MCP detectors, and the signal from 10 revolutions was summed. The signal here is most probably due to dissociation and not electron emission, although it is hard to exclude thermionic emission. However, the electron emission clearly does not occur directly from the excited state, as we do not sample neutral products until 30 μs after...
photoexcitation. The two spectra reveal a band with a maximum between 430 nm and 450 nm that we ascribe to a higher-lying $\pi-\pi^*$ state based on calculations (vide infra). As the prompt signal was highest at 420 nm, this shows that direct electron detachment does indeed occur to produce neutral products. The probability of detachment is increased as the population of the excited state, which acts as a doorway state to the continuum, increases.

Excitation Energy Calculations

To shed light on the lowest-energy transitions of the phenolate of 4, we subjected it to a computational study. The geometry was optimized with MP2/TZVPP, and electronic excitation energies were calculated using the CC2 \cite{2} and SORCI \cite{23} methods with the aug-cc-pVDZ basis set. The coupled-cluster CC2 method was used in earlier studies on nitrophenolates \cite{3}, where it predicted the lowest $\pi-\pi^*$ transition to be 0.02–0.22 eV above the experimental absorption maximum. SORCI is a multi-reference method, similar to the CASPT2 method. It is more suitable for the selective description of resonant $\pi-\pi^*$ excitations, which CC2 tends to mix with artificial Rydberg excitations that appear in the same energy region. Both methods agree that the S0–S1 transition is a HOMO–LUMO ($\pi-\pi^*$) transition with strong CT character and with an energy of 0.99 eV (1252 nm; SORCI) or 1.63 eV (761 nm; CC2), and therefore outside the energy window of the gas-phase measurements. The calculated oscillator strength for this transition is very small (0.01 in both methods), consistent with frontier orbital plots showing that the HOMO and LUMO orbitals overlap only weakly (Figure 5). When comparing the CC2 CT absorption of the phenolate of 4 (760 nm) to that previously calculated for the linearly conjugated stilbene derivative (608 nm, 2.04 eV) \cite{2a} (see Figure 5, top, and Figure 6), it transpires that cross-conjugation does indeed cause a significant redshift in the transition of the phenolate of 4. The predicted S0–S2 transition of the phenolate of 4 is described as an $n-\pi^*$ transition at 2.52 eV (492 nm) by CC2. The SORCI spectrum of $\pi-\pi^*$ transitions further reveals that the lowest transitions with significant oscillator strengths are higher-lying $\pi-\pi^*$ transitions, which SORCI predicts at energies of 2.70 and 2.86 eV (459 and 434 nm, respectively), close to the peak seen in the experimental gas-phase spectrum. Similar transitions are found in the CC2 spectrum when diffuse functions are excluded from the basis set. Under these conditions, Rydberg-like transitions are shifted to higher energies, but also valence excitation energies are overestimated. We calculated a vertical detachment energy (VDE) of 2.86 eV (434 nm) with the CEPA/1 method \cite{23}. Hence, the higher-lying $\pi-\pi^*$ transitions may be excitations into resonant states.

It is noteworthy that the optimized structure of the phenolate of 4 does not adopt a fully coplanar conformation, as this indicates that electronic communication in the cross-conjugated system is not strong enough to overcome modest steric strain. Thus, the two aryl groups are rotated by dihedral angles of 43° (nitrophenyl) and 26° (phenolate) relative to the ethylene bridge.

For the phenolate of the cross-conjugated and planar diethynylethene compound 1, the CC2 method provides absorptions at 886 nm (1.40 eV; oscillator strength 0.06) and 499 nm (2.49 eV; oscillator strength 0.35). The decoupling of the donor and acceptor ends by the cross-conjugated spacer is reflected in the small oscillator strength of the CT transition at 886 nm, and is consistent with the HOMO and LUMO presented in Figure 5 (bottom). For the phenolate of linearly conjugated diethynylethene $E$–$Z$, absorption maxima of 736 nm (1.69 eV; oscillator strength 1.90) and 420 nm (2.95 eV; oscillator strength 0.38) are obtained. Thus, again we see a significantly lower CT excitation en-
ergy for the cross-conjugated species, although the difference (0.3 eV) is smaller than that obtained between the ethylene-bridged chromophores (0.4 eV). The results are summarized in Figure 6. By comparing the two linearly conjugated phenolates, we see that the longer diethynylethene bridge causes a lower CT excitation energy. This dependence on the distance between donor and acceptor ends is consistent with studies on push–pull-conjugated oligomers (HOMO–LUMO gap decreasing with donor–acceptor separation).

Likewise, the excitation energy of the cross-conjugated phenolate of E-2 is lower than that of 4.

Solution-Phase Fluorescence Spectroscopy

The fluorescent properties of the chromophores were also investigated. Notably, cross-conjugated chromophores 1 and 4 did not show any significant emission in the range 350–850 nm, and 2 and 3 showed a weak emission. Neutral fluorene derivative 5 showed a stronger emission at 588 nm, which was redshifted to 740 nm for the phenolate (Figure 7). The fluorescence characteristics of the compounds are summarized in Table 2. The absence of fluorescence for the cross-conjugated compounds indicates ultrafast internal conversion (IC) to a lower-lying “dark” state, consistent with the existence of a CT state.

Table 2. Fluorescence characteristics of compounds in MeOH; emission maxima (λem, fluorescence) and quantum yields (φfl).

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>E-2</td>
<td>368</td>
<td>556</td>
<td>n.a.</td>
<td>8 × 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>366</td>
<td>516</td>
<td>n.a.</td>
<td>6 × 10^{-4}</td>
</tr>
<tr>
<td>5</td>
<td>372</td>
<td>588</td>
<td>740</td>
<td>4 × 10^{-3}</td>
</tr>
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</table>

[a] Corresponding to sodium phenolate (obtained by 1% NaOMe); n.a.: not applicable.

Conclusions

In conclusion, we have developed protocols for the synthesis of a variety of nitrophenolate chromophores bridged by either linearly or cross-conjugated bridges. Due to the weak coupling provided by cross-conjugated bridges, the HOMO–LUMO CT absorption (S0–S1) was either absent or very weak in the solution-phase absorption spectra of these compounds. This interpretation was supported by quantum chemical calculations on the phenolates of 1 and 4, which have cross-conjugated ethylene and diethynylethene bridges between the phenolate and nitrobenzene units. The validity of the theoretical predictions of 4 was ascertained by comparing the calculated higher-energy transition to that observed experimentally in the gas phase. In addition, the calculations show that the electronic decoupling between the donor and the acceptor ends does indeed result in lower-energy HOMO–LUMO gaps for the phenolates of 1 and 4 relative to those of linearly conjugated analogues, consistent with our previous results on cross-conjugated m-nitrophenolate vs. linearly conjugated o,p-nitrophenolates. The most significant difference is seen between nonplanar and planar 1,1- and 1,2-diarylethylenes. Finally, while the linearly conjugated chromophores were weakly fluorescent, the cross-conjugated ones were found to be nonfluorescent, which indicates an ultrafast internal conversion to a low-lying “dark” state (CT state).

Experimental Section

General Methods: Chemicals were used as received from suppliers. All metal-catalysed reactions were performed under an atmosphere of argon in argon-flushed solvents. Dry THF was distilled from sodium, and dry CH2Cl2 was obtained from a solvent purification system from Innovative Technology, Inc. Flash column and dry column vacuum chromatography were performed on silica gel (ROCC 40–62 μm and 15–40 μm, respectively). Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel 60F (Merck 5554). NMR spectra were recorded with a 500 MHz Bruker instrument with a cryoprobe. The residual solvent signal was used for calibration (CDCl3: δ = 7.26 and 77.16 ppm for 1H and 13C, respectively). Electrospray (ESI) mass spectra were recorded with a Micromass Q-TOF mass spectrometer (for HRMS) with polyethylene glycol (PEG) as internal standard, or with a Bruker Micro-TOF Q II mass spectrometer. Gas chromatography (GC) mass spectra were recorded with an Agilent 6890A (G1530A) gas chromatograph coupled with an Agilent mass-selective detector 5973 Network. Melting points were determined with a Stuart SMP 40 automatic melting point apparatus. IR spectra were obtained with a Bruker ALPHA-P spectrometer using the “ATR platinum Diamond 1 Refl” accessory. Peaks are listed with relative intensities: v (very weak), w (weak), m (medium), s (strong). Elemental analyses were obtained at the microanalysis laboratory at the Department of Chemistry, University of Copenhagen.

UV/Vis absorption spectra were measured with a Cary 50 UV/Vis spectrophotometer at a concentration of 10^{-5} m in methanol in a quartz cuvette with a path length of 1 cm. Fluorescence measurements were performed on a Fluorolog-3 (Jobin Yvon Horiba) spectrophotometer in methanol at room temperature. The fluorescence quantum yields were determined considering 9,10-diphenylanthracene as a standard (φ0 = 0.95). Gas-phase spectroscopy was carried out using the ELectrostatic Ion Storage ring in Aarhus (ELISA), as described in detail pre-
The sample was dissolved in methanol and ionised using the electrospray method. Ions were accumulated in a 22-pole ion trap filled with helium buffer gas (room temperature). The ion trap was emptied ten times per second to produce ion bunches. After acceleration to 22 keV energies, ions of interest were selected using an electromagnet and injected into the ring, where they were stored. The revolution time in the ring was 60 µs. After 24 ms, the ions were irradiated with light from an EKSPLA laser, which is an Nd:YAG laser operated at 10 Hz. Its 1064 nm output was frequency tripled to 355 nm, and this light was sent through an optical parametric oscillator (OPO) to produce visible and infrared light.

The reaction mixture was then concentrated in vacuo and the residue was partitioned between water and CH2Cl2. The combined organic extracts were dried with Na2SO4, and the solvent was removed under reduced pressure. Flash column chromatography (SiO2, CH2Cl2) gave 1 (38 mg, 56%) as a yellow solid, m.p. 176–177 °C. IR (ART): ν = 3397 (m), 2925 (w), 2850 (w), 2195 (w), 1592 (m), 1505 (s), 1339 (s), 1265 (m), 1165 (m 1098 m), 849 (s), 830 (s), 747 (m), 668 (m), 529 (m) cm−1. 1H NMR (500 MHz, CDCl3): δ = 8.19 (d, J = 9.0 Hz, 2 H), 7.61 (d, J = 9.0 Hz, 2 H), 7.39 (d, J = 8.8 Hz, 2 H), 6.80 (d, J = 8.8 Hz, 2 H), 4.84 (s, 1 H), 2.68–2.59 (m, 4 H), 1.74–1.60 (m, 6 H) ppm. 13C NMR (126 MHz, CDCl3): δ = 163.23, 155.78, 146.93, 133.33, 132.23, 130.71, 130.21, 129.34, 127.56, 116.70, 98.74, 92.04, 91.52, 89.35, 84.08, 33.34, 33.25, 27.99, 27.89, 26.26 ppm. HRMS (ESI): calculated for C22H18NO4Si [M – H]+, m/z = 436.62 found 436.62.

(E)-4-[6-(4-Nitrophenyl)hexa-3-en-1-yl]phenyl Benzoate (E-1): A mixture of vinyl bromide E-13 (173 mg, 0.686 mmol), alkyne (126 mg, 0.882 mmol), PdCl2(PPh3)2 (24 mg, 0.034 mmol), and Cu (7 mg, 0.04 mmol) was degassed and a degassed mixture of toluele (10 mL) and iPr2NH (3.5 mL) was added. The mixture was stirred for 3.5 h at room temp, then saturated aqueous ammonium chloride (30 mL) was added, and the mixture was then extracted with CH2Cl2 (40 mL). The organic phase was washed with brine (20 mL), dried with Na2SO4, and concentrated in vacuo. Flash column chromatography (SiO2, heptane/CH2Cl2, 1:2) gave E-14 (235 mg, 87%) as a bright yellow solid. Trace amounts of the Z-isomer could be removed by recrystallization from MeCN, m.p. 170–173 °C (decomp.). 1H NMR (500 MHz, CDCl3): δ = 8.25–8.17 (m, 4 H), 7.68–7.63 (m, 1 H), 7.63–7.58 (m, 2 H), 7.57–7.47 (m, 4 H), 7.23 (d, J = 8.7 Hz, 2 H), 6.39 (d, J = 16.0 Hz, 1 H), 6.30 (d, J = 16.0 Hz, 1 H) ppm. 13C NMR (126 MHz, CDCl3): δ = 164.82, 151.31, 147.15, 133.84, 132.99, 132.30, 130.23, 129.74, 129.20, 128.66, 128.62, 128.26, 128.04, 120.25, 119.66, 95.61, 93.04, 92.65, 87.85 ppm. HRMS (ESI): calculated for C23H16NO4 [M – H]+, m/z = 394.1074; found 394.1078.

(E)-4-[6-(4-Nitrophenyl)hexa-3-en-1-yl]phenyl (E-2): Ester E-14 (100 mg, 0.254 mmol) was dissolved in CH2Cl2 (20 mL) and MeOH (20 mL). K2CO3 (50 mg, 0.36 mmol) was added, and the mixture was stirred for 5 h. Saturated aqueous NH4Cl (40 mL) was added, the phases were separated, and the aqueous phase was extracted with CH2Cl2. The combined organic extracts were washed with brine, dried with Na2SO4, and concentrated in vacuo.

Flash column chromatography (SiO2, heptane/CH2Cl2, 1:2) gave E-2 (43 mg, 59%) as an orange solid, m.p. 191–195 °C (decomp.). IR (ART): ν = 3414 (vw), 3106 (vw), 2910 (w), 2766 (s), 1604 (w), 1569 (s), 1338 (m), 1271 (m), 1159 (m 1099 m), 929 (s), 852 (s), 830 (m), 748 (m), 687 (m), 533 (m) cm−1. 1H NMR (500 MHz, CDCl3): δ = 8.20 (d, J = 9.0 Hz, 2 H), 7.59 (d, J = 9.0 Hz, 2 H), 7.37 (d, J = 8.8 Hz, 2 H), 6.81 (d, J = 8.8 Hz, 2 H), 6.37 (d, J = 15.9 Hz, 1 H), 6.23 (d, J = 15.9 Hz, 1 H) ppm. 13C NMR (126 MHz, CDCl3): δ = 156.37, 147.21, 133.67, 132.37, 130.02, 129.72, 128.37, 127.56, 127.25, 126.81, 126.72, 126.68, 126.62, 126.40, 125.29, 124.99, 124.85, 124.71, 123.74, 123.62, 122.94, 122.81, 122.74, 122.55, 122.44, 121.33, 119.66, 119.62, 119.51, 119.46, 118.92, 117.78, 117.54, 117.44, 117.34, 117.03, 116.76, 116.64, 97.84, 92.04, 91.52, 89.35, 84.08, 33.34, 33.25, 27.99, 27.89, 26.26 ppm. HRMS (ESI): calculated for C22H16NO4 [M – H]+, m/z = 356.1292; found 356.1304.

2-(2-Chlorophenyl)propanoic acid (12): A mixture of alkyne (10) (231 mg, 0.713 mmol), PdCl2(PPh3)2 (25 mg, 0.036 mmol), and Cu (7 mg, 0.04 mmol) was degassed and degassed THF (20 mL) and iPr2NH (2.5 mL) were added. The mixture was stirred for 4 h, then the solution was removed in vacuo, Et2O was added and, after filtration, the mixture was concentrated. Flash column chromatography (SiO2, heptane/CH2Cl2, 1:2) gave 12 (303 mg, 92%) as a yellow solid, m.p. 49.5–50.2 °C (decomp.). 1H NMR (500 MHz, CDCl3): δ = 8.24–8.16 (m, 4 H), 7.70–7.59 (m, 3 H), 7.59–7.49 (m, 4 H), 7.21 (d, J = 8.7 Hz, 2 H), 2.74–2.57 (m, 4 H), 1.77–1.59 (m, 6 H) ppm. 13C NMR (126 MHz, CDCl3): δ = 164.89, 163.98, 150.81, 146.84, 133.72, 132.72, 132.13, 130.47, 130.21, 129.30, 128.64, 123.58, 121.86, 120.91, 97.54, 91.60, 90.83, 89.39, 85.43, 33.26, 33.20, 27.86, 27.77, 26.09 ppm. MS (FAB+): m/z = 461.62 [M + H]+. C26H25NO2 (461.51) calcd. C 78.07, H 5.02, N 3.03; found C 77.74, H 4.90, N 3.04.
123.81, 123.42, 118.75, 115.80, 115.09, 96.70, 93.48, 92.42, 86.89 ppm. HRMS (ESI+): calced. for C19H10NO3 [M – H]– 288.0666; found 288.0672. C19H11NO3 (289.28): calcd. C 74.40, H 3.55, N 4.56.

-4-[(4-Nitrophenyl)buta-1,3-diyin-1-yl]phenyl Benzoate (16): To a degassed mixture of toluene (5 mL) and iPr2NH (2 mL) was added a mixture of alkyne 12 (149 mg, 0.67 mmol), chloroalkyne 15 (102 mg, 0.56 mmol), PdCl2(PPh3)2 (20 mg, 0.028 mmol), and CuI (5 mg, 0.026 mmol). The mixture was stirred at room temp. for 3 h. Saturated aqueous NH4Cl (20 mL) was added, and the mixture was extracted with CH2Cl2 (40 mL), washed with brine (25 mL), dried with Na2SO4, and concentrated in vacuo. The sample was purified by dry column vacuum chromatography (SiO2, CH2Cl2:MeOH, 10:1) to give 4 (250 mg, 52%) as a yellow solid, m.p. 125–128 °C. IR (ART): v = 3434 (m), 3049 (w), 2927 (w), 1590 (s), 1512 (s), 1496 (s), 1338 (s), 1316 (s), 1272 (s), 1205 (s), 1175 (s), 1107 (m), 937 (s), 908 (s), 860 (m), 833 (s), 801 (m), 768 (m), 710 (s), 506 (s) cm–1. 1H NMR (500 MHz, CDCl3): δ = 8.19 (d, J = 8.9 Hz, 2 H), 7.49 (d, J = 8.9 Hz, 2 H). 7.18 (d, J = 8.7 Hz, 2 H), 6.82 (d, J = 8.7 Hz, 2 H), 5.55 (d, J = 0.7 Hz, 1 H), 5.48 (d, J = 0.7 Hz, 1 H), 4.79 (s, 1 H) ppm. 13C NMR (126 MHz, CDCl3): δ = 155.87, 148.55, 147.95, 147.46, 133.14, 130.69, 121.78, 121.63, 116.07, 115.48 ppm. MS (ESI+): m/z = 240.0 [M – H]+. C19H11NO3 (241.24): calcd. C 69.70, H 4.60, N 5.81; found C 69.48, H 4.38, N 5.56.

7-Nitro-9H-fluoren-2-ol (5): Amine 19 (340 mg, 1.51 mmol) was heated at 100 °C for 15 min with H2SO4 (2.5 mL, 6 mol). Then acetic acid (25 mL) was added, and the mixture was boiled further until the yellow ammonium sulfide had dissolved. The ammonium sulfate was next obtained in a finely divided form by rapidly cooling the solution to 0 °C while stirring. NaNO2 (440 mg, 6.38 mmol) in water (5.5 mL) was added to the stirred suspension at 0 °C, and the temperature was raised to 80 °C and kept there for 2 h. Then, sulfamic acid was added to the bright yellow suspension until no gas was formed upon addition. The mixture was cooled to 0 °C, and H2SO4 (440 mg, 6.38 mmol) in water (6 mL) was added to the stirred suspension at 0 °C, and the temperature was raised to 80 °C for 2.5 h. The yellow solid isolated from the cooled mixture was washed with aqueous NaHCO3. Recrystallization from AcOH gave 5 (115 mg, 34%) as an orange solid, m.p. 225–228 °C (decomp.); ref[98] 241–251 °C. IR (ART): v = 3407 (w), 1608 (m), 1583 (s), 1508 (s), 1454 (s), 1393 (m), 1309 (s), 1288 (s), 1102 (m), 1274 (s), 914 (s), 852 (m) cm–1. 1H NMR (500 MHz, [D6]DMSO): δ = 0.90 (d, J = 2.0 Hz, 1 H), 8.23 (dd, J = 8.4, 2.0 Hz, 1 H), 7.92 (d, J = 8.4 Hz, 1 H), 7.35 (d, J = 8.3 Hz, 1 H), 7.05 (d, J = 2.2 Hz, 1 H), 6.87 (dd, J = 8.3, 2.2 Hz, 1 H), 3.97 (s, 2 H) ppm. 13C NMR (126 MHz, [D6]DMSO): δ = 159.58, 148.56, 147.54, 147.75, 143.29, 131.29, 128.93, 121.90, 121.09, 118.81, 115.19, 115.24, 36.42 ppm. HRMS (ESI+): calcd. for C19H13NO3Na+ [M + Na]+ 250.0475; found 250.0463.

Supporting Information (see footnote on the first page of this article): Experimental details for the synthesis of 12, absorption spectra for the E-Z/Z-2 mixture, gas-phase absorption spectrum of the phe- nolate of 4 without corrections for laser power, copies of 1H and 13C NMR spectra of all compounds.

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