

CHEMISTRY A European Journal



Accepted Article Title: Linear and Star-Shaped Extended Di- and Tristyrylbenzenes: Synthesis, Characterization and Optical Response to Acid and Metal lons Authors: Hao Zhang, Eugen A. Kotlear, Soh Kushida, Steffen Maier, Frank Rominger, Jan Freudenberg, and Uwe Heiko Bunz This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.202000893 Link to VoR: http://dx.doi.org/10.1002/chem.202000893 **Supported by** ACES



Linear and Star-Shaped Extended Di- and Tristyrylbenzenes: Synthesis, Characterization and Optical Response to Acid and Metal lons

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Abstract: Two linear 1,4-distyrylbenzenes and five star-shaped 1,3,5-tristyrylbenzene derivatives ($L_{2a}-L_{2b}$, Y_0-Y_3 and Y_{NBu}) were synthesized and spectroscopically characterized. The photophysical properties, optical response to acid and metal ions were investigated. Upon backbone extension of linear distyrylbenzenes or the introduction of dibutylanilines, the electronic spectra are red-shifted. Incorporation of electron-deficient pyridyl units does not significantly affect the optical properties. Variation of the number of pyridine rings and substitution pattern tune the fluorescence response to acids and metal ions. The novel arenes discriminate Al³⁺, Mn²⁺, Fe³⁺, Fe²⁺, Cd²⁺, Ag⁺ and Hg²⁺.

Introduction

Functional π-conjugated chromophores with linear^[1] or starshaped geometry^[2] are relevant responsive materials.^[3] 1,3,5-Tristyrylbenzene^[4] is an excellent core for dendritic molecules.^[2c, 5] Peripheral and core substitution allow tuning of photoluminescence^[6] and mesogenic behavior.^[2b]

Manipulation of the substituents in X-shaped molecules leads to disjunct frontier molecular orbitals and tunable optical properties.^[7] If pyridines or dialkylanilines are incorporated, they become acidochromic.^[8] Both size and symmetry of the conjugated system affect the properties and performance in applications.^[5c, 9] We describe the synthesis, photophysical characterization, and acid/metal ion response of two linear 1,4-distyryl (L_{2a} and L_{2b}) and five star-shaped styrylbenzene derivatives (Y₀-Y₃ and Y_{NBu}).

Results and Discussion

Synthesis, X-ray crystallographic analyses and liquid crystalline behavior

 L_{2a} is a distyrylbenzene substituted with two pyridines. L_{2b} was designed as an analogue of L_{2a} with a longer effective conjugation length^[10]. Y_0 is a star-shaped and C_3 -symmetric π -system bearing three identical arms. Based on this known

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skeleton (Y₀) reported by Maier *et al.*,^[5c] Y₁₋₃ and Y_{NBu} are obtained either by variation of the number of pyridine rings or the introduction of electron-rich dibutylaniline groups, respectively (Scheme 1).

1 was reacted with 1-bromohexane (K₂CO₃, anhydrous DMF) to afford 2, which was transformed by a Bouveault reaction to the monoaldehyde 3. Heck coupling between 3 and three arylethylenes produced 4-6, which were in turn subjected to a Horner reaction with triphosphonate 7 in the presence of sodium hydride, thus, affording Y_0 (77%), Y_3 (33%) and Y_{NBu} (68%). As reference systems, distyrylbenzene L2a was obtained after Heck reaction of **2** and 4-vinylpyridine (45%). To obtain π -extended L_{2b}, 8 was subjected to an Arbuzow reaction with triethyl phosphite, followed by a Horner reaction with monoaldehyde 5. L_{2b} was isolated after column chromatography on silica gel (82%). Y_1 and Y_2 were obtained via two one-pot procedures starting from 7 with aldehydes 5 and 4. For Y₁, the first Horner reaction of 7 with monoaldehyde 5 (molar ratio: 1:1.1) afforded 10, which was subjected to a second Wittig-Horner reaction with 4 in situ (28% over two steps). By changing the stoichiometry of 7 and 5 (1:2.2), Y_2 was isolated by a similar two-step routine with a yield of 44%. It should be noted that potassium tert-butoxide as a base did not work.^[11]. L_{2a}-L_{2b} and Y₀-Y₃ are yellow or orange solids, while Y_{NBu} is a yellow oil. All styrylbenzene derivatives (SBs) are well soluble in common organic solvents.

We obtained single crystals for Y_0 (from DCM/methanol), L_{2b} and Y_3 (from DCM/*n*-hexane) and performed X-ray analysis. Figure 1 depicts the structure and Table S1–S3 summarize the corresponding data. As shown in Figure S1, all of derivatives are almost planar and their vinylic linkers display *E*-configuration. However, the packing patterns of L_{2b} , Y_0 and Y_3 deviate significantly from each other. L_{2b} packs in parallel layer stacks with some displacement. Y_0 displays a 2-dimensional wall-like arrangement and the orientation of molecular planes in adjacent parallel walls is different. In Y_3 , a pattern of parallel planes was observed, which extends in three directions.

Similar to Maier's star-shaped compounds, nematic liquid crystalline phases from isotropic during cooling scans were observed for Y_{0-2} as investigated by temperature-dependent polarization optical micrographs (Figure S2).^[5c] No liquid crystalline behaviour was detected for oily Y_{NBu} at room temperature.

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Scheme 1. Synthetic route to linear 1,4-distyrylbenzenes (L_{2a}-L_{2b}) and star-shaped 1,3,5-tristyrylbenzene derivatives (Y₀-Y₃ and Y_{NBu}).



Figure 1. Single crystal structures of L_{2b} , Y_0 and Y_{3} .

Photophysical properties and theoretical calculations

The normalized absorption and emission spectra of the compounds in dilute THF are shown in Figure 2. Table 1 summarizes the photophysical data. Due to the *meta*-conjugation, absorption spectra of star-shaped series Y_0 - Y_3 are superimposable to that of L_{2a} , with a maximum absorption

centered at around 400 nm and a shoulder peak located at 326-348 nm. It is mainly attributed to the extension of conjugation or the electron-rich dibutylaniline groups.

In THF, the trend in the emission maxima (Figure 2b) follows the order $Y_{NBu}>L_{2b}>L_{2a}>Y_3>Y_2>Y_1>Y_0.$ L_{2b} exhibits a redshifted green emission with a vibronic structure relative to that of $L_{2a},$ owing to its longer conjugation length. Asymmetric Y_1 and Y_2 show similar emission maxima in comparison to symmetric Y₃ while their maxima are redshifted by ca. 10 nm compared to symmetric hydrocarbon $Y_{0.}$ The fluorescence maximum of Y_{NBu} bathochromically shifted to 519 nm (Stokes shift of 4151 cm⁻¹). The large Stokes shift observed for Y_{NBu} is caused by its higher dipole moment in its excited state stabilized in more polar solvents.^{[12]} $L_{2a\text{-}2b}$ and $Y_{0\text{-}3}$ display quantum yields ($\Phi_{\text{f}})$ varying from 0.64 to 0.82, while Y_{NBu} exhibits a green fluorescence with a quantum yield of 0.61. Although $Y_{0\text{-}3}$ and Y_4 have similar conjugation skeletons, dibutylamine-containing Y_4 shows lower quantum yield, which might be attributed to the free intramolecular rotation or the existence of photoelectron transfer facilitated by the flexible dibutylamine groups.[13]

Density functional theory (DFT) calculations (B3LYP/6-31++G**)^[14] provide further insight into optoelectronics. The calculated HOMO-LUMO energy gaps for L_{2a}-L_{2b}, Y₀-Y₃ and Y_{NBu} are in the range from 2.56 to 3.06 eV (Figure S3). The lower gaps of Y_{NBu} or L_{2b} are a result of the extended conjugation, resulting in distinct bathochromic shifts in the electronic absorption spectra. These results, as well as the trend of absorption maxima calculated by TDDFT methods (Figure S3) are consistent with the experiment.

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Figure 2. Normalized UV/vis absorption (a) and emission (b) spectra of SBs in THF.

Table	1. Photo	ohysical d	ata (in T	HE) and	calculated	energy ga	ps for SBs
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Compounds	λ _{abs} [nm] ^a	λ _{max,em} [nm]	QY ^b	τf [ns]	λ _{st} [nm]/Δυ _{st} [cm ⁻¹] ^c	calcd energy gap [eV, nm]			
L_{2a}	329 (2.37), 400 (2.88)	461	0.64	2.00	61, 3308	3.06, 405			
L _{2b}	432 (7.31)	485	0.68	1.10	53, 2529	2.56, 484			
Y ₀	329 (6.17), 401 (11.0)	447	0.82	1.39	46, 2566	2.97, 417			
Y ₁	330 (5.68), 403 (9.89)	454	0.73	1.51	51, 2787	2.86, 433			
Y ₂	331 (7.13), 405 (12.4)	456	0.72	1.52	51, 2761	2.87, 432			
Y ₃	348 (2.29), 401 (2.86)	457	0.79	1.67	56, 3118	2.96, 418			
Y _{NBu}	326 (1.91), 427 (8.64)	519	0.61	1.41	92, 4151	2.82, 440			

^a Measured in THF and extinction coefficients ($\mathcal{E}_{max} \times 10^4 \, \text{M}^{-1} \cdot \text{cm}^{-1}$) are shown in parentheses. ^b QY = quantum yield. ^c $\Delta v_{st} = 1/\lambda_{abs} - 1/\lambda_{em}$.

Fluorochromicity



Figure 3. Photograph of SBs in different solvents under a hand-held black light with illumination at 365 nm.

Figure 3 shows the emission behaviors of SBs in solvents with different polarity. Negligible changes are observed in the emission color of L_{2a} and Y₁₋₃ with pyridine rings. L_{2b} and Y_{NBu}, emit red-shifted with increasing solvent polarity.^[12] The effect of solvents on the emission features was evaluated by the Lippert–Mataga plot^[15] (Supporting Information). All of the SBs displayed linear dependence of Δv on Δf together with different slopes. L_{2b} and T_{NBu} showed a much larger slope (Figure S5 and Table S5). The

slope of the fitting line for Y_{NBu} is highest, up to 9673 cm⁻¹, comparable to that of the X-shaped distyrylbenzenes,^[16] which further indicated its larger dipole moment changes between the ground and excited states ($\mu_e\text{-}\mu_g$), leading to the pronounced solvent sensitivity.^[17]

Optical response to protons

Pyridines or dibutylanilines are basic, all SBs (except Y_0) and display an acidochromic change of their absorption and emission spectra (Figure 4). SBs with pyridine units experience a red-shift, accompanied with a loss of fluorescence intensity. Upon protonation the donor-acceptor character of these SBs increases and therefore internal charge transfer is favored. The addition of TFA to Y_{NBu} leads to strongly blue emissive species, in which the dibutylamino groups are protonated and the HOMO is stabilized by protonation, resulting in an increased HOMO-LUMO gap. The color change is detected by eye. As expected, Y_3 is more sensitive to protonation compared to Y_1 and Y_2 , as there are three pyridine rings as interaction sites.

As shown in Figure 5, when -log [TFA] of approx. 1.30 is reached (c = 50 mM), **Y**₃ shows a red-shifted absorption (30 nm) and a 100 nm red shift and distinct attenuation of its emission. With excess acid (c = 500 mM, -log [TFA] < 1.0), the original absorption band of **Y**_{NBu} at around 427 nm diminished and a new distinct band formed at 338 nm. A blue shift in emission of $\Delta\lambda$ = -69 nm was observed.



Figure 4. Photograph of SBs in THF ($c = 4 \mu g/mL$) with increasing content of TFA under a hand-held black light with illumination at 365 nm (inset data: the number of equivalents of TFA).

Figure 5. Normalized UV/vis absorption (left) and emission (right) spectra for the titrations of Y_3 (top) and Y_{NBu} (down) in THF with different concentration of TFA.

Optical response to metal ions

Dilute solutions of all the SBs in DCM were exposed to an excess of salts of 13 cations (Al³⁺, Zn²⁺, Cu²⁺, Cu⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cd²⁺, Ag⁺, Pb²⁺ and Hg²⁺, added as perchlorates,

and Cul) (Figure 6a). Only Hg²⁺ quenches luminescence of Y₀. Except for Zn²⁺, Cu²⁺, Ni²⁺, the addition of the remaining ten metal ions leads to either quenching or a red shift in emission of SBs with pyridine units (L_{2a}, L_{2b} and Y₁₋₃). In the case of Y_{NBu}, Al³⁺, Mn²⁺, Fe³⁺, Fe²⁺, Cd²⁺, Ag⁺, and Hg²⁺ induce a blue shift in emission, as expected for a coordination at the aniline nitrogen. Al³⁺, Mn²⁺, Cd²⁺ and Co²⁺ are quenchers for Y₁ and Y₂, but they less impact photoluminescence of Y₃. Al³⁺, Mn²⁺, Fe³⁺, Fe²⁺, Cd²⁺, Ag⁺ and Hg²⁺ can be easily distinguished from each other through the responses of the SBs by the naked eye. It is challenging to discriminate Cd²⁺ from Zn²⁺.^[18] SBs with pyridine or dibutylaniline groups display fluorescence response in the presence of Cd²⁺ but no response with Zn²⁺.

$$\boldsymbol{\sigma}_{m,n}(r,g) = \sqrt{\frac{\sum_{SBS1}^{SBS7}(r_n - r_m)^2 + (g_n - g_m)^2}{3^{*7}}}$$
(1)

Statistical evaluation of differences in emission colors after exposure to metal ions was performed. Figure 6b shows the autocorrelation plot of their response. The brightness independent color coordinates rg of the RAW data of the photographs were determined and treated with MANOVA statistics (eq. 1).^[7c, 19] Zn²⁺, Cu²⁺ and Ni⁺ are hard to discern due to their weak coordination and thus have similar color responses. All of the other investigated metal ions are distinguished.

Conclusion

We have synthesized linear 1,4-distyryl and star-shaped 1,3,5tristyrylbenzene derivatives ($L_{2a}-L_{2b}$, Y_0-Y_3 and Y_{NBu}). These are strongly fluorescent in dilute solutions. Y_{NBu} works as polarity sensor due to its response to different solvents. Upon protonation, all of the pyridine-containing $L_{2a}-L_{2b}$ and Y_0-Y_3 compounds show a pronounced red shift, and the fluorophore with dibutylaniline groups Y_{NBu} displays a blue shift in emission. Ten metal ions such as Al³⁺, Mn²⁺, Fe³⁺, Fe²⁺, Cd²⁺, Ag⁺ and Hg²⁺ were well discriminated.

* Zn2+ Cu2+ Cu* Mn2+ Fe

Aq

Ha

Cd2+ Ag* Pb2+ Hg2

0.00

0.07

0.10

0.17

0.23

0.29

Figure 6. (a) Exposure of all the SBs (10 µM) to different metal cations in DCM. Photographs were taken under a hand-held black light (365 nm) with a digital camera; (b) Autocorrelation plot (RAW rg values) of all the SBs in DCM after exposure to metal ions.

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Experimental Section

General Procedure 1 (GP1): Synthesis of intermediates **4-6** by Heck reaction. The reaction was performed in a heat-gun-dried 50 mL Schlenk tube under a nitrogen atmosphere. The brominated intermediate (1.0 eq) and the vinyl compound (1.14 eq) were dissolved in dry DMF. Pd(OAc)₂ (5 mol%), tris(*o*-tolyl)phosphine (0.1 eq) and dry triethylamine (0.8 mL) were added and the mixture was stirred at 110 °C for 48 h. After the reaction mixture was cooled to ambient temperature, it was poured into water to give a suspension which was extracted with DCM. The combined organic layers were washed with brine, dried over MgSO₄ and the solvents were removed under reduced pressure. The residues were purified by column chromatography.

General Procedure 2 (GP2): Synthesis of symmetric Y_0 , Y_3 and Y_{NBu} by Wittig-Horner reaction. Under nitrogen atmosphere, the triphosphonate **7** (1.0 eq) was dissolved in dry THF and the solution was cooled to 0 °C. NaH (15.0 eq) was added carefully and the mixture was stirred at 0 °C for 40 min before the monoaldehyde **4-6** (4.5 eq) was added slowly. The reaction mixture was then allowed to warm to RT and further stirred for 3 days. After removing THF on a rotary evaporator, the residues were purified on silica gel column.

4,4'-((1E,1'E)-(2,5-bis(hexyloxy)-1,4-phenylene)bis(ethene-2,1-

diyl))dipyridine (L2a). Under nitrogen atmosphere, a solution of 2 (218 mg, 500 µmol), 4-vinylpyridine (118 mg, 1.20 mmol), Pd(OAc)₂ (11.2 mg, 50 µmol), tris(o-tolyl)phosphine (30.4 mg, 100 µmol) and triethylamine (1.20 mL) in dry DMF (10 mL) was stirred at 110 °C for 48 h. After the reaction mixture was cooled to ambient temperature, it was poured into water to give a suspension which was extracted with DCM. The combined organic layers were washed with brine dried over MgSO4 and the solvents were removed under reduced pressure. The residues were purified by column chromatography (silica gel, DCM/EE = 5:1, $R_{\rm f}$ = 0.21) and afforded L_{2a} as a yellow solid (110 mg, 225 µmol, 45%). M.p.: 135-136 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.58 (d, J = 6.0 Hz, 4H), 7.70 (s, 1H), 7.64 (s, 1H), 7.38 (d, J = 6.0 Hz, 4H), 7.18 - 7.08 (m, 3H), 7.05 (s, 1H), 4.08 (t, J = 6.5 Hz, 4H), 1.95 - 1.82 (m, 4H), 1.63 - 1.49 (m, 4H), 1.47 – 1.33 (m, 8H), 0.93 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 150.1, 149.8, 145.4, 129.7, 128.3, 128.2, 127.6, 126.9, 126.7, 126.5, 126.0, 123.6, 121.0, 114.6, 114.1, 111.2, 110.9, 69.7, 31.8, 29.5, 26.1, 22.8, 14.2. IR (cm⁻¹): 2942, 2915, 2360, 1592, 1476, 1209, 1028, 968, 850, 803, 596, 525. HRMS (MALDI): m/z [M+H]+ calcd for $C_{32}H_{41}N_2O_2$ 485.3168, found 485.372.

2,5-Bis(hexyloxy)-4-(2-(pyridin-4-yl)vinyl)benzaldehyde (5). According to **GP1** a solution of monoaldehyde **3** (385 mg, 1.00 mmol), 4-vinylpyridine (214 mg, 1.14 mmol), Pd(OAc)₂ (11.2 mg, 50.0 µmol), tris(*o*-tolyl)phosphine (30.4 mg, 100 µmol) and triethylamine (0.7 mL) in DMF (10 mL) was stirred at 110 °C for 48 h. Column chromatography (silica gel, PE/EA = 5:1, $R_{\rm f}$ = 0.20) afforded **5** as a yellow viscous oil (343 mg, 840 µmol, 84%). ¹H NMR (300 MHz, CDCl₃) δ 10.59 (s, 1H), 8.73 (d, *J* = 5.2 Hz, 2H), 7.78 (d, *J* = 16.5 Hz, 1H), 7.52 (d, *J* = 5.6 Hz, 2H), 7.47 (s, 1H), 7.30 (t, *J* = 8.2 Hz, 2H), 4.24 (t, *J* = 6.5 Hz, 2H), 4.16 (t, *J* = 6.5 Hz, 2H), 2.11 – 1.90 (m, 4H), 1.72 – 1.27 (m, 14H), 1.05 (dd, *J* = 6.4, 4.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 189.1, 156.0, 151.1, 150.2, 144.7, 132.7, 129.4, 127.6, 125.1, 121.1, 111.3, 110.3, 69.3, 69.2, 31.6, 29.2, 25.9, 22.7, 14.1. IR (cm⁻¹): 2928, 2857, 1676, 1601, 1422, 1206, 1018, 529. HRMS (DART): m/z [M+H]⁺ calcd for C₂₆H₃₆NO₃ 410.2690, found 410.2687.

4-(4-(Dibutylamino)styryl)-2,5-bis(hexyloxy)benzaldehyde (6). According to **GP1** a solution of monoaldehyde **3** (771 mg, 2.00 mmol), 4dibutylaminostyrene (509 mg, 2.20 mmol), Pd(OAc)₂ (22.4 mg, 100 μmol), tris(*o*-tolyl)phosphine (60.9 mg, 200 μmol) and triethylamine (1.5 mL) in DMF (20 mL) was stirred at 110 °C for 48 h. Column chromatography (silica gel, PE/EA = 20:1, R_1 = 0.50) afforded **6** as a yellow viscous oil (582 mg, 1.10 mmol, 54%). ¹H NMR (400 MHz, CDCl₃) δ 10.42 (s, 1H), 7.41 (d, J = 8.7 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.25 – 7.03 (m, 3H), 6.67 – 6.40 (m, 3H), 4.17 – 3.93 (m, 4H), 3.39 – 3.20 (m, 4H), 1.91 – 1.74 (m, 4H), 1.63 – 1.47 (m, 8H), 1.42 – 1.26 (m, 12H), 0.92 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 189.4, 189.2, 156.6, 155.8, 151.1, 150.5, 148.5, 147.7, 136.2, 135.9, 132.9, 132.8, 130.5, 128.5, 124.5, 123.9, 123.7, 123.4, 120.7, 117.6, 114.8, 111.7, 111.1, 110.2, 109.9, 109.7, 69.4, 69.3, 50.9, 31.7, 29.7, 29.4, 26.0, 22.8, 20.5, 14.2, 14.1. IR (cm⁻¹): 2955, 2928, 2870, 1682, 1612, 1519, 1466, 1366, 1214, 1186, 811. HRMS (DART): m/z [M+H]⁺ calcd for C₃₅H₅₄NO₃ 536.4098, found 536.4101.

1,3,5-Tris((E)-2,5-bis(hexyloxy)-4-((E)-styryl)styryl)benzene (Y₀). According to GP2 a solution of triphosphonate 7 (42.3 mg, 80.0 µmol) in dry THF (8 mL) was treated with NaH (28.8 mg, 1.20 mmol) and monoaldehyde 4 (105 mg, 256 µmol) was added. The crude product was purified by column chromatography (silica gel, PE/EA = 20:1, $R_{\rm f}$ = 0.41) to yield the desired compound Y_0 as a yellow green powder (79.6 mg, 61.6 μmol, 77%). M.p.: 110-111 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.66 -7.49 (m, 15H), 7.39 (t, J = 7.6 Hz, 6H), 7.32 - 7.22 (m, 6H), 7.22 - 7.14 (m, 9H), 4.11 (dd, J = 15.1, 6.6 Hz, 12H), 1.99 - 1.85 (m, 12H), 1.59 (td, J = 13.5, 7.0 Hz, 12H), 1.48 - 1.34 (m, 24H), 0.93 (dt, J = 25.7, 6.8 Hz, 18H). 13 C NMR (150 MHz, CDCl₃) δ 151.3, 151.2, 138.7, 138.1, 129.0, 128.9, 128.7, 127.5, 127.1, 126.6, 124.1, 123.6, 111.0, 110.8, 69.7, 31.7, 29.5, 26.1, 22.8, 14.2. IR (cm⁻¹): 2926, 2856, 2360, 1419, 1199, 958, 750, 690, 598, 506. HRMS (MALDI): m/z [M]+ calcd for C₉₁H₁₁₄O₆ 1290.8615, found 1290.947.

1,3,5-Tris((E)-2,5-bis(hexyloxy)-4-((E)-2-(pyridin-4-

yl)vinyl)styryl)benzene (Y3). According to GP2 a solution of triphosphonate 7 (42.3 mg, 80.0 µmol) in dry THF (8 mL) was treated with NaH (28.8 mg, 1.20 mmol) and monoaldehyde 5 (114.7 mg, 280 µmol) was added. The crude product was purified by column chromatography (silica gel, DCM/MeOH = 50:1, $R_{\rm f}$ = 0.35) to yield the desired compound Y_3 as an orange solid (34.9 mg, 26.9 µmol, 33%). M.p.: 122-123 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.58 - 8.50 (d, J = 5.4 Hz, 6H), 7.71 - 7.39 (m, 12H), 7.23 - 6.63 (m, 15H), 4.01 - 3.93 (m, 12H), 1.91 – 1.83 (m, 12H), 1.58 (m, 12H), 1.39 – 1.27 (m, 24H), 0.96 – 0.89 (m, 18H). ¹³C NMR (150 MHz, CDCl₃) δ 151.9, 151.5, 151.4, 150.8, 150.4, 149.9, 145.6, 139.0, 138.8, 130.4, 130.3, 129.9, 128.5, 128.3, 126.3, 126.2, 125.7, 125.6, 124.6 124.3, 124.2, 121.1, 115.9, 111.3, 111.0, 109.6, 69.9, 69.7, 68.8, 32.2, 31.9, 29.9, 29.7, 26.3, 26.2, 22.9, 14.4. IR (cm⁻¹): 2925, 2856, 2320, 1591, 1498, 1416, 1204, 966, 803, 517. HRMS (MALDI): m/z [M+H]+ calcd for C₈₇H₁₁₂N₃O₆ 1295.8629, found 1295.8624.

4,4',4"-((1*E*,1'*E*,1'E)-(((1*E*,1'*E*,1'*E*)-benzene-1,3,5-triyltris(ethene-2,1diyl))tris(2,5-bis(hexyloxy)benzene-4,1-diyl))tris(ethene-2,1-

diyl))tris(N,N-dibutylaniline) (YNBu). According to GP2 a solution of triphosphonate 7 (42.3 mg, 80.0 µmol) in dry THF (8 mL) was treated with NaH (28.8 mg, 1.20 mmol) and monoaldehyde 6 (137 mg, 256 µmol) was added. The crude product was purified by column chromatography (silica gel, PE/DCM = 2:1 + 2% triethylamine, $R_{\rm f}$ = 0.45) to yield the desired compound Y_{NBu} as an orange viscous oil (90.9 mg, 54.3 µmol, 68%).¹H NMR (600 MHz, CDCl₃) δ 7.61 – 7.37 (m, 5H), 7.33 (d, J = 8.4 Hz, 4H), 7.26 - 7.03 (m, 11H), 7.03 - 6.89 (m, 4H), 6.82 - 6.65 (m, 1H), 6.62 - 6.15 (m, 7H), 4.16 - 3.60 (m, 12H), 3.18 (m, 12H), 1.92 - 1.63 (m, 12H), 1.48 (m, 24H), 1.41 - 1.26 (m, 24H), 1.25 - 1.07 (m, 12H), 0.95 -0.73 (m, 36H). ¹³C NMR (150 MHz, CDCl₃) δ 153.4, 151.4, 150.8, 147.8, 146.5, 138.9, 131.0, 130.3, 129.2, 128.6, 128.4, 128.3, 127.9, 127.7, 125.9, 125.8, 125.3, 124.3, 124.1, 118.4, 115.4, 114.0, 112.6, 112.0, 111.7, 111.2, 110.1, 69.8, 50.9, 31.8, 29.6, 27.8, 26.1, 22.8, 20.5, 16.0, 14.2. IR (cm⁻¹): 2953, 2926, 2857, 1607, 1519, 1366, 1185, 1030, 962, 805, 523. HRMS (MALDI): m/z [M+H]⁺ calcd for C₁₁₄H₁₆₅N₃O₆ 1673.2777, found 1673.293. Elemental analysis calcd. (%) for C114H165N3O6: C 81.82; H 9.94; N 2.51; found: C 81.60, H 10.76, N 2.45.

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1,4-Bis((E)-2,5-bis(hexyloxy)-4-((E)-2-(pyridin-4-

yl)vinyl)styryl)benzene (L2b). Under a nitrogen atmosphere, the bisphosphonate 9 (45.4 mg, 120 µmol) was dissolved in dry THF (10 mL) and the solution was cooled to 0 °C. NaH (28.8 mg, 1.20 mmol) was added carefully and the mixture was stirred at 0 °C for 40 min before monoaldehyde 5 (103 mg, 252 µmol) was added slowly. The reaction mixture was then allowed to warm to RT and further stirred for 2 days. After removing THF on a rotary evaporator, the residues were purified on silica gel column (silica gel, PE/EA = 20:1, $R_{\rm f}$ = 0.19) to yield the desired compound L_{2b} as an orange solid (87.9 mg, 98.9 µmol, 82%). M.p.: 147-148 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (m, 4H), 7.68 (d, J = 16.4 Hz, 2H), 7.61 - 7.42 (m, 6H), 7.38 (d, J = 6.0 Hz, 3H), 7.22 - 6.97 (m, 9H), 4.20 - 3.74 (m, 8H), 1.99 - 1.73 (m, 8H), 1.70 - 1.48 (m, 8H), 1.50 -1.21 (m, 16H), 1.09 – 0.80 (m, 12H). 13 C NMR (150 MHz, CDCl₃) δ 151.7, 151.1, 150.2, 149.7, 145.4, 137.3, 129.2, 128.3, 128.2, 127.0, 126.0, 125.5, 124.1, 123.2, 120.9, 111.1, 110.5, 69.6, 31.7, 29.6, 29.5, 26.1, 22.8, 14.2. IR (cm⁻¹): 2931, 2853, 1590, 1397, 1207, 1034, 961, 847, 726, 525. HRMS (MALDI): m/z [M]+ calcd for C₆₀H₇₆N₂O₄ 888.5805, found 888.5835.

4-((E)-4-((E)-3,5-bis((E)-2,5-bis(hexyloxy)-4-((E)-styryl)styryl)-2,5-bis(hexyloxy)styryl)pyridine (Y1). Under a nitrogen atmosphere, the triphosphonate 7 (42.3 mg, 80 µmol) was dissolved in dry THF (10 mL) and the solution was cooled to 0 °C. NaH (28.8 mg, 1.2 mmol) was added carefully and the mixture was stirred at 0 °C for 40 min before monoaldehyde 5 (35.4 mg, 86.8 µmol) was added slowly. The reaction mixture was stirred overnight at room temperature. After removing THF in vacuo, the residues containing 10 were dried and used in the next step without further purification. To a solution of 10 in dry THF (8 mL) was added NaH (28.8 mg, 1.20 mmol) at 0 °C. The mixture was stirred at 0 °C for 40 min, and then another monoaldehyde 4 (71.9 mg, 176 µmol) was added. The reaction mixture was then allowed to warm to RT and further stirred for 2 days. After removing THF on a rotary evaporator, the crude product was purified by column chromatography (silica gel, PE/EA = 1:1, $R_{\rm f}$ = 0.49) to yield the desired compound Y₁ as an orange solid (29.8 mg, 23.1 µmol, 28% over two steps). M.p.: 71-72 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.69 (d, J = 5.8 Hz, 2H), 7.82 (d, J = 16.4 Hz, 1H), 7.74 - 7.60 (m, 12H), 7.49 (m, 6H), 7.37 (dd, J = 16.3, 7.8 Hz, 4H), 7.34 - 7.23 (m, 9H), 7.19 (d, J = 16.4 Hz, 1H), 4.20 (dt, J = 10.9, 6.5 Hz, 12H), 2.07 -1.98 (m, 12H), 1.74 - 1.66 (m, 12H), 1.57 - 1.47 (m, 24H), 1.08 - 0.99 (m, 18H). 13 C NMR (150 MHz, CDCl₃) δ 151.8, 151.2, 150.1, 145.5, 138.8, 138.5, 138.0, 129.8, 128.9, 128.7, 128.4, 128.31, 127.5, 127.0, 126.6, 125.9, 125.5, 124.3, 123.6, 120.9, 111.0, 110.7, 69.7, 31.7, 29.5, 26.1, 22.8, 14.2. IR (cm⁻¹): 2925, 2856, 2359, 1590, 1420, 1202, 1029, 960, 690, 507. HRMS (MALDI): m/z [M+H]+ calcd for C89H114NO6 1292.8646, found 1292.963.

4,4'-({5-[(E)-2-{2,5-bis(hexyloxy)-4-[(E)-2-

phenylethenyl]phenyl}ethenyl]-1,3-phenylene}bis{[(*E*)ethene-2,1diyl][2,5-bis(hexyloxy)-4,1-phenylene](*E*)ethene-2,1-diyl}dipyridine

(Y₂). Under a nitrogen atmosphere, the triphosphonate **7** (42.3 mg, 80.0 µmol) was dissolved in dry THF (8 mL) and the solution was cooled to 0 °C. NaH (28.8 mg, 1.20 mmol) was added carefully and the mixture was stirred at 0 °C for 40 min before monoaldehyde **5** (70.8 mg, 174 µmol) was added slowly. The reaction mixture was stirred overnight at room temperature. After removing THF on a rotary evaporator, the residues containing **11** were dried and used in the next step without further purification. To a solution of **11** in dry THF (8 mL) was added NaH (28.8 mg, 1.20 mmol) at 0 °C. The mixture was stirred at 0 °C for 40 min, and then another monoaldehyde **4** (36.1 mg, 88.0 µmol) was added. The reaction mixture was then allowed to warm to RT and further stirred for 2 days. After removing THF on a rotary evaporator, the crude product was purified by column chromatography (silica gel, EE/MeOH = 50:1, $R_{\rm I}$ = 0.58) to yield the desired compound **Y**₂ as an orange solid (46.4 mg, 35.8 µmol, 44% over two steps). M.p.: 121–122 °C. ¹H NMR (600 MHz,

CDCl₃) δ 8.70 (d, *J* = 5.8 Hz, 4H), 7.81 (d, *J* = 16.4 Hz, 2H), 7.75 – 7.58 (m, 9H), 7.56 – 7.45 (m, 6H), 7.42 – 7.32 (m, 4H), 7.27 (m, 7H), 7.19 (d, *J* = 16.4 Hz, 2H), 4.21 (m, 12H), 2.10 – 1.90 (m, 12H), 1.82 – 1.62 (m, 12H), 1.62 – 1.42 (m, 24H), 1.04 (m, 18H). ¹³C NMR (150 MHz, CDCl₃) δ 151.7, 151.3, 151.2, 150.2, 145.4, 138.8, 138.6, 138.0, 129.7, 128.9, 128.8, 128.3, 128.2, 127.6, 127.2, 126.9, 126.6, 126.1, 125.6, 124.3, 124.1, 123.6, 120.9, 111.1, 110.8, 69.7, 31.7, 29.6, 26.1, 22.8, 14.2. IR (cm⁻¹): 2926, 2856, 2360, 1589, 1419, 1203, 962, 690, 527. HRMS (MALDI): m/z [M+H]⁺ calcd for C₈₈H₁₁₃N₂O₆ 1293.8599, found 1293.919.

Crystallographic data: CCDC 1959608 (L_{2b}), CCDC 1959609 (Y_0), and CCDC 1959610 (Y_3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

Acknowledgements

H. Z. is grateful to the CSC (Chinese Scholarship Council) for a fellowship.

Keywords: Sensing • Tristyrylbenzene • Acidochromicity • Optical Response • Metal Ions

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Linear and Star-Shaped Extended Diand Tristyrylbenzenes: Synthesis, Characterization and Optical Response to Acid and Metal Ions

A series of extended star-shaped tristyrylbenzenes has been developed. Their optoelectronic properties can be tuned via the aryl terminus, which make them useful sensors for protons or metal ions.