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Imine Formation as a Simple Reaction to Construct Copper-Reactive Cruciform Fluorophores

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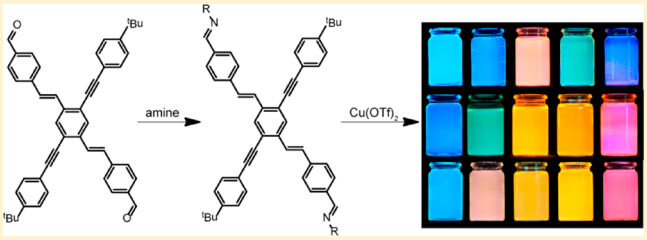
Supporting Information

ABSTRACT: We developed a series of new conjugated cruciform fluorophores (XF) featuring imine groups. The condensation of an XF containing aldehyde functionalities and selected primary amines leads to several XF-imine derivatives. Upon addition of Cu^{2+} or Zn^{2+} ions to solutions of the imine XFs in different solvents, a red-shifted emission is detected, resulting in an altered emission color. The imine acts as a simple modular metallo-reactive fluorophore.



INTRODUCTION

Cross-shaped aromatic species[1−5] can be competent, operationally functional, reactive fluorophores.[6−11] We have specifically investigated 1,4-distyryl-2,5-bis(arylethynyl)benzenes (XF) as attractive targets. Having a unified and modularized synthesis, XFs can be deployed in amine sensing[12] and differentiation of organic acids[13] but are also metallo reactive, particularly if they carry dialkylamino or pyridine functions on their traverses. Consequently, consanguine groups of XFs with smoothly tunable properties to detect and/or discern one or a group of analytes should be easily created. Here, we introduce a surprisingly simple way to postfunctionalize aldehyde-substituted XFs into metallo-responsive fluorophores by simple addition of different primary amines and formation of imines.

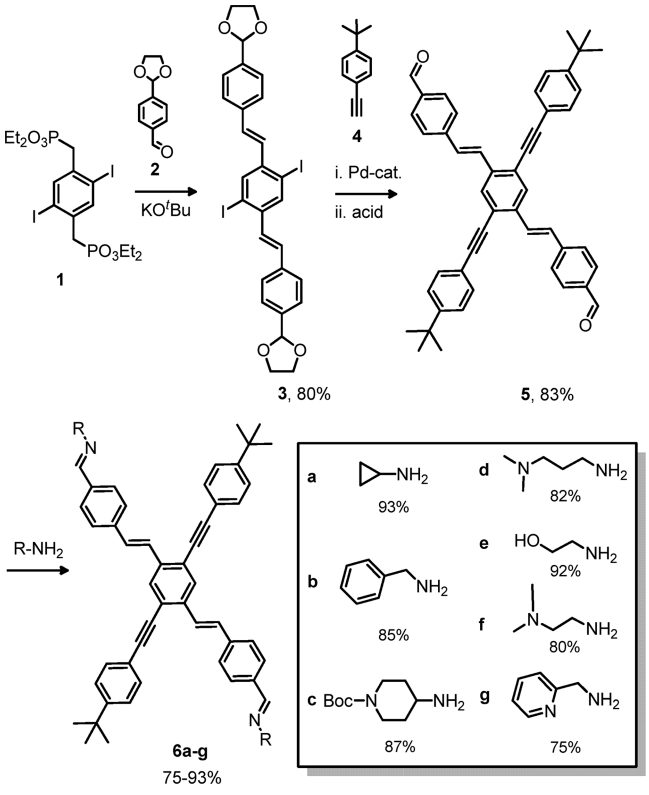
The difference in response of an analyte class to one fluorophore often leads to ambiguities in the identification of a specific analyte; however, the usage of several consanguine fluorophores allows easier identification of an analyte, allowing discrimination. On the other hand, to develop a unique response to a specific fluorophore it is also advantageous to have fluorophore libraries with similar properties (same functional group) but with differential responses to closely related analytes.[14]

To sense amines, we have employed an aldehyde-functionalized donor-acceptor XF or an aldehyde-substituted distyrylbenzene experiencing fluorescence turn-on upon exposure.[15,16] Fluorescence turn-on was due to the rapid formation of the imine. Consequently, aldehydes such as **5** are transformed into functional imines when treated with suitable primary amines. Here we present a series of seven consanguine XF-based imines that display a ratiometric signal when exposed to Cu^{2+} or Zn^{2+} salts. Their color change (and concomitant spectroscopic changes) is dependent upon the used amine, i.e., the formed imine. The metallo response of the XF is tailored in the last, post-functionalization step. In principle, this approach is attractive for the generation of functional fluorophores.

RESULTS AND DISCUSSION

Scheme 1 displays the synthesis of the platform **5**. Starting from **1**,[17,18] a Horner reaction with **2** gives rise to the formation of **3** in

Scheme 1. Synthesis of Seven Different Imines 6a−g Starting from the Bisaldehyde 5



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80% yield. Sonogashira reaction of **3** with **4** and deprotection furnishes the light yellow dialdehyde **5** in a total yield of 75%; **5** can be prepared in gram quantities but is reactive. It gives the dimethyl acetal after 1 day, when dissolved in methanol, even without the addition of acid. When **5** is dissolved in the amines **a**–**g**, the imines **6a**–**g** form smoothly. While chromatography leads to hydrolysis, the imines are purified by precipitation from methanol and/or crystallization; **6a**–**g** give the correct NMR spectroscopic data. The imines **6** are only weakly solvatochromic, as expected for acceptor-substituted distyrylbenzene derivatives (Figure 1, top row, small strips).

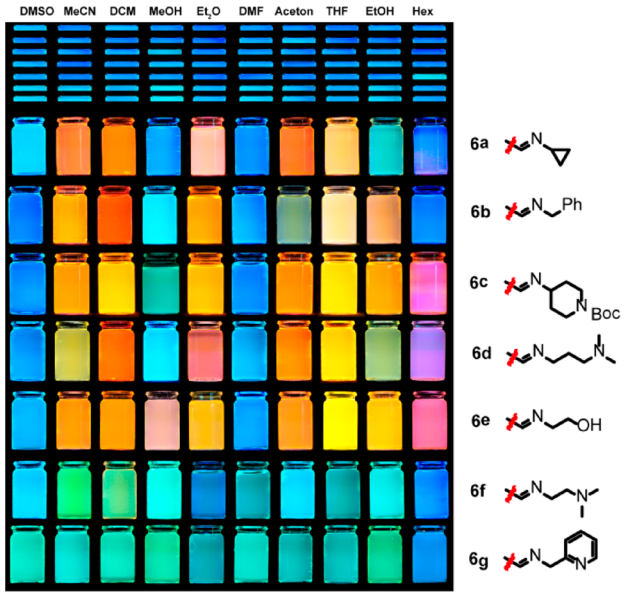

Figure 1. Addition of an excess of $Cu(OTf)_2$ to solutions of the modularly synthesized imines **6a**–**g** in different solvents. The top row displays solutions of the imines **6a**–**g** without the added metal cations. All of the solutions are blue fluorescent and therefore only shown as small segments. The concentration of the imines **6a**–**g** is 10 μM in the different solvents. The fluorescence intensity of the blue solutions is stronger than the emission of the orange or yellow solutions by a factor of 10–20. For clarity, the vials have been photographed such that the color hues are most realistically depicted, *not* according to the intensity of emission.

In a simplistic way, imines are vinylogous to pyridines. As a consequence, we imagined that coordination of metal cations to derivatives of **6** should lead to red-shifted (and weakened) emission. Addition of $Cu(OTf)_2$ to **6b** in different solvents (Figure 1) resulted in emission color changes. Red shift and decline of intensity of the emission are visible in acetonitrile, DCM, THF, and ethanol. For $Zn(OTf)_2$ a similar red shift of the emission and decreased intensity are observed (see the Supporting Information, Figure S1). When compared to each other, the imines show fewer color changes with $Zn(OTf)_2$ than upon addition of $Cu(OTf)_2$. The imine **6d**, featuring an additional coordinating dimethylamino group, gives brightly colored responses when Cu^{2+} or Zn^{2+} salts are added. The addition of $Cu(OTf)_2$ to **6d** in THF leads to yellow fluorescence. The addition of additional pyridine units is a successful strategy to increase the binding affinity of fluorophores to zinc ions[19,20] resulting in a stronger color change imine in **6g**. The color of solutions of **6g** changes from blue to green-yellow with Zn^{2+} and with Cu^{2+} to green-turquoise.

From Figure 1 some trends can be gleaned. If an excess of $Cu(OTf)_2$ is used, imines **6a**–**g** give a color reaction in all solvents with exception of methanol, DMSO, and DMF. Hexanes are problematic, but for reasons of lack of solubility of the metal salt and the coordinated fluorophore. The imines **6a**–**e** change color from blue to yellow or orange, when $Cu(OTf)_2$ is coordinated. The imines **6f** and **6g**, however, only display a slight shift in color even when exposed to a large excess of $Cu(OTf)_2$. Both imines share a formal 1,2-diamine as common structural element. A possible reason for the decreased emission wavelength shift is the combination of electronegative (–I) and coordination effects of the nitrogen substituents, which simultaneously effective, lead to a lowered positive partial charge on the imine nitrogen, when coordinating to Cu^{2+} ions. This leads to a counterintuitive situation that strong binding is accompanied by a small ratiometric signal.

How do substituents attached to the imine nitrogen affect the binding to the metal cations? We investigated **6b**–**g** in the presence of $Cu(OTf)_2$ acetonitrile. Figure 2 displays the absorption and emission spectra of the XF-imines **6b**–**g** in acetonitrile before (thick black line) and after (red line) the addition of $Cu(OTf)_2$. The XFs themselves without the metal salts have roughly all the same absorption and emission characteristics. To observe metal binding, we added 100 equiv of $Cu(OTf)_2$ to a 1 μM solution of XF in acetonitrile observing the unbound and the bound species with an additional band in the absorption spectra for **6b**, **6c**, and **6e**. The absorption spectra of **6d**, **6f**, and **6g** did not change for reasons that are not entirely clear.[6–11] Excitation at an isosbestic point shows for **6b**, **6c**, and **6e** a new band appearing at around 600 nm in the emission for **6d** and **6g** quenching and for **6f** increased fluorescence intensity. If the excitation wavelength is chosen to be in the new absorption region, emission spectra of the low intensity band at 600 nm were recorded for **6b**–**f**.

Table 1 displays the spectroscopic data of the imines **6b**–**g** and their metal adducts from Figure 2. The major component of the fluorescent lifetimes is around 0.8–2.5 ns for all of the imine fluorophores **6b**–**g**, quite typical for distyrylbenzene derivatives.[11,21] The emission lifetime changes differently for the fluorophores upon coordination of copper; **6b**, **6c**, and **6e** display similar τ_{fl} = 1.8–1.9 ns for their Cu-bound forms. The emission decreases and is red-shifted when going from the uncoordinated to the coordinated form. Along, the lifetimes of both signals shorten. The addition of $Cu(OTf)_2$ to the solution of derivatives **6d**, **6f**, and **6g** changes their fluorescent intensity but increases their fluorescence lifetime.

To obtain more precise information about the binding abilities of our imines, we performed titrations of **6b**–**g** with copper(II)triflate (XF concentration 1.0 μM). We selected wavelengths of increasing or decreasing signals in both absorption and emission spectra to obtain the binding constant (Figure 3). As we have not been able to extract a good model for the stoichiometry of metal cation and XF, the log β obtained by the fit eq 1 is an approximate but appropriate substitute for binding constant values with one type of imine nitrogen for coordination:[22,23]

$$I(x) = I_{start} + \frac{I_{end} - I_{start}}{1 + 10^{(\log \beta - x)n}} \quad (1)$$

$I(x)$ is the relative intensity (absorption or fluorescence) at a given copper concentration $[Cu^{2+}]$, x is the negative logarithm of the copper concentration $-\log [Cu^{2+}]$ and I_{start} and I_{end} are the relative intensities at the beginning and the end of the titration. Log β is at the inflection point, where the difference of intensity

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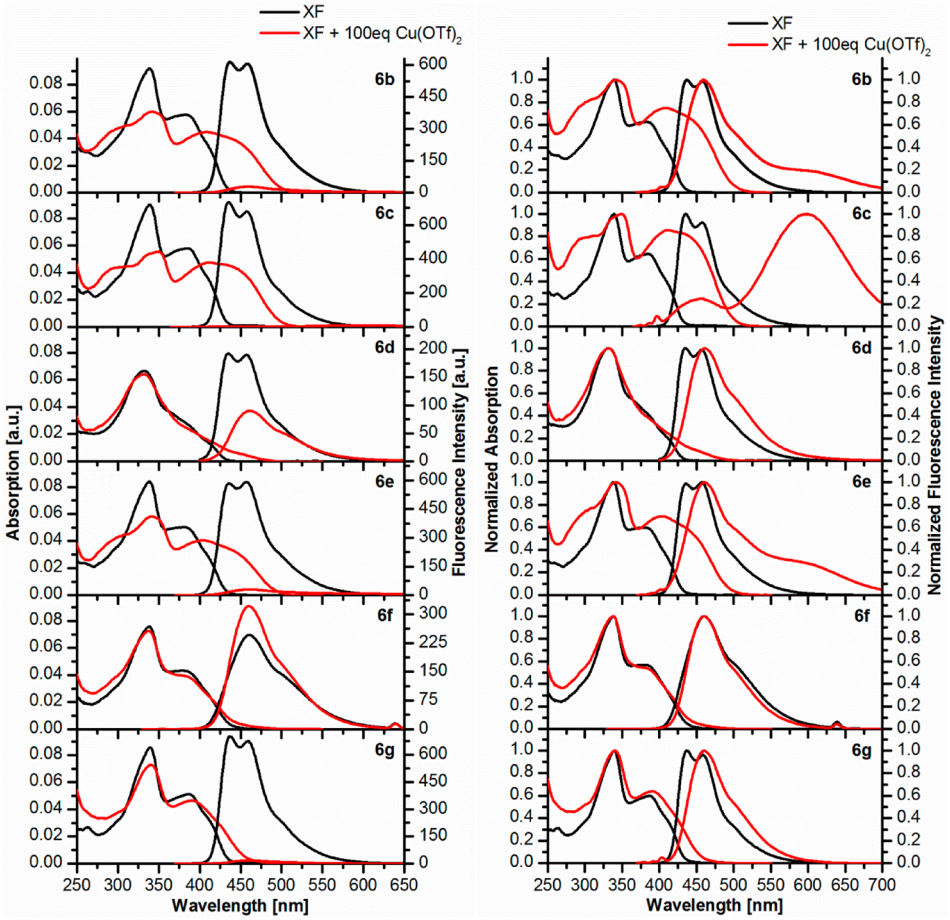

Figure 2. Addition of 100 equiv of $Cu(OTf)_2$ to solutions of **6b–g** in acetonitrile. (Left) Absorption and emission spectra with their measured intensities. (Right) Normalized absorption and emission spectra. Emission spectra were recorded with the excitation at the isosbestic point.

Table 1. Photophysical Properties of Imines 6b–g in Acetonitrile and in the Presence of $Cu(OTf)_2$

compd	$\lambda_{max\ abs}$ (nm)	$\lambda_{max\ abs}$ (+ 100 equiv of Cu^{2+}) (nm)	$\lambda_{max\ em}$ (nm)	$\lambda_{max\ em}$ (+ 100 equiv of Cu^{2+}) (nm)	λ_{em}[a] (nm)	τ (ns)	τ (+ 1000 equiv of Cu^{2+}) (ns)
6b	339, 383	341, 410	437, 458	459, 590sh	460	1.82	1.57, 2.76
					600	1.83	0.43
6c	339, 384	350, 410	435, 457	457, 598	460	1.77	0.72, 2.59
					600	1.81	0.52
6d	332	331	435, 458	461	470	1.03	1.97, 3.26
6e	338, 382	342, 403	435, 458	461, 600sh	460	1.92	1.21, 2.70
					600	1.88	0.54
6f	338, 379	338, 382sh	461	460	460	0.79, 2.53	2.33, 3.23
6g	339, 386	340, 390	437, 459	461	460	1.80	2.19, 3.17

[a]Excitation wavelength 376 nm.

of I_{start} and I_{end} is half. The value n describes the slope of the curve and does not necessarily correlate with the stoichiometry of the formed complex.

Table 2 displays the parameter log β for **6b–g** resulting from the nonlinear least-squares fit of selected experimental data. Some of the titration plots of **6d** and **6f** display a different shape. Therefore, eq 1 could not be used for fitting those data. For these curves a sigmoidal fitting function with two possible inflection points was applied (see the Supporting Information), or these curves were not used at all. From these nonlinear least-squares fits only the first log β was used. This value is in good accordance with the other log β values resulting from fits using eq 1. The log β value describes the binding of the imine XF to copper. All log β values of the derivatives are between 5.1 and 6.0. Having only the imine nitrogen, **6b** has the smallest log β (average 5.35). Having additional heteroatoms for **6c–g**, the average log β values increases to 5.77 (**6f**) and 5.96 (**6d, 6g**). Both values indicate that the presence of a chelating nitrogen increases the binding significantly. Consequently, the imine **6g** formed from picolylamine is particularly efficient in the detection of copper cations as suggested by the work of Urano et al. for other pyridine containing ligands.[21]

CONCLUSIONS

We efficiently prepared seven consanguine, fluorescent imines **6a–g** in one step by reaction of amines **a–g** with the dialdehyde

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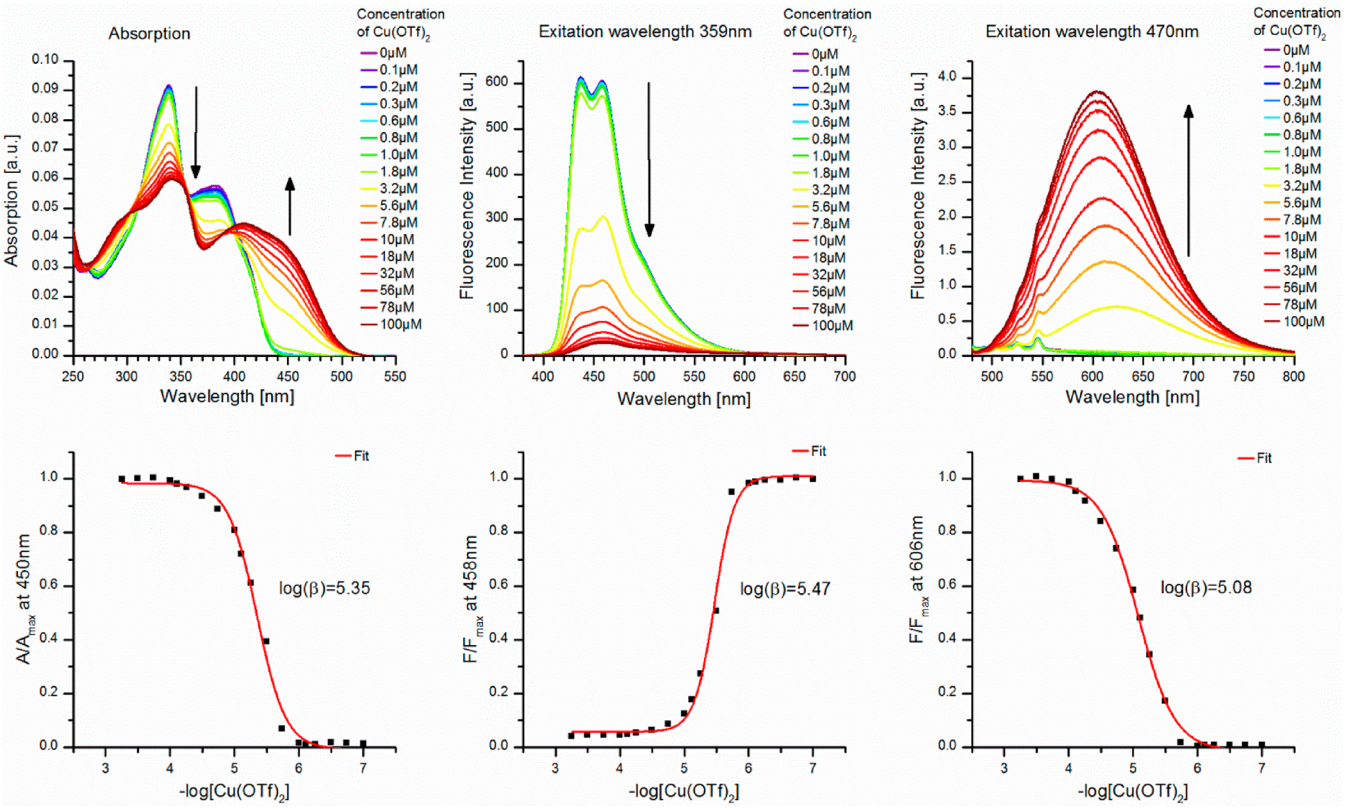

Figure 3. (Top) Absorption spectra and emission spectra recorded with different excitation wavelengths for the titration of **6b** with $Cu(OTf)_2$. (Bottom) Relative titration plots from the absorption and emission spectra for selected wavelengths (solid squares) and the nonlinear least-squares fit (red line) of the experimental data to eq 1.

Table 2. Binding Data Obtained from the Titration for Selected Wavelengths of Absorption and Emission Data

6b	log β	**6c**	log β	**6e**	log β
Abs (nm) 300	5.53	292	5.60	290	5.43
Abs (nm) 450	5.35	450	5.63	450	5.54
Em (nm) 458[a]	5.47	457[c]	5.80	458[d]	5.68
Em (nm) 650[a]	5.30	625[c]	5.37	650[d]	5.39
Em(nm) 606[b]	5.08	600[b]	5.18	600[b]	5.30
6d	log β	**6f**	log β	**6g**	log β
Abs (nm) 292	6.04	290	5.80	300	5.82
Abs (nm) 450	5.97	450	5.87	440	6.02
Em (nm) 675[e]	6.09	635[b]	5.64	460[g]	6.05
Em (nm) 650[f]	5.74				

[a]Excitation wavelength 359 nm. [b]Excitation wavelength 470 nm. [c]Excitation wavelength 355 nm. [d]Excitation wavelength 358 nm. [e]Excitation wavelength 390 nm. [f]Excitation wavelength 455 nm. [g]Excitation wavelength 360 nm.

5. The imines form readily in good to excellent yields and display attractive and tunable binding to Cu^{2+} and Zn^{2+} salts in THF or in acetonitrile. Coordination leads to a significant red shift in emission, suggesting that imines **6** are potentially attractive ratiometric fluorophores. The absorption and emission red shift and weakening of emission in the imines upon metalation is easily understood when looking at the imines as vinylogous pyridines. Metal binding leads to the stabilization of the LUMO, but influences the position of the HOMO much less. Using different aromatic mono- or dialdehydes in combination with suitable amines should allow to generate a whole family of modularly constructed metal-reactive fluorophores. It did not escape our notice that this modular system should be useful for the synthesis of *any* type of reactive fluorophore that can be constructed by a sensory appendage and a fluorescent nucleus using imine formation.[24,25]

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded on 250 and 300 MHz spectrometers. ^{13}C NMR spectra were recorded on a 75 MHz spectrometer. The HRMS measurements were performed using systems with quadruple ionic trap or time-of-flight mass spectrometers. Time-correlated single photon counting lifetime measurements were made using a pulsed laser diode (wavelength 376 nm).

1,4-Diiodo-(*E*)-2,5-bis(4-(1,3-dioxolan-2-yl)styryl)benzene (3): Compound **1** (3.40 g, 19.0 mmol) was dissolved in water-free THF (150 mL) under N_2 atmosphere. Then **2** (6.00 g, 9.5 mmol) and KO^{t}Bu (2.00 g, 19.0 mmol) were added at 0 °C. The reaction mixture was stirred for 2 h at 22 °C. Hydrolysis and centrifugation, washing with methanol, gave **3** (5.10 g, 80%): mp 265 °C dec; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.14 (s, 2H), 7.59 (d, J = 8.18 Hz, 4H), 7.48 (d, J = 7.80 Hz, 4H), 7.25 (d, J = 16.31 Hz, 2H), 7.04 (d, J = 16.01 Hz, 2H), 5.79 (s, 2H), 4.15−3.99 (m, 8H); ^{13}C NMR: the solubility of **3** was too low to obtain a spectrum; IR (cm^{-1}) 2946, 2868, 1606, 1455, 1426, 1382, 1361, 1332, 1298, 1284, 1240, 1219, 1175, 1112, 1086, 1039, 1014, 984, 958, 943, 925, 888, 872, 856, 834, 810, 730, 721, 655, 621, 609, 535, 502, 483, 460, 437, 420, 401; HRMS (EI) m/z calcd for $C_{28}H_{24}I_2O_4$ $[M]^+$ 677.9764, found 677.9744.

1,4-Bis(4-*tert*-butylphenylethynyl)-(*E*)-2,5-bis(4-formylstyryl)-benzene (5): In a dried Schlenk flask **3** (2.43 g, 3.60 mmol) was added to a degassed solution of NEt_3 (2.00 mL) in water free THF (250 mL) under N_2 atmosphere. The mixture was dissolved by heating. After cooling, **4** (1.70 g, 10.7 mmol), $Pd(PPh_3)_2Cl_2$ (50.0 mg, 71.2 μmol), and CuI (14.0 mg, 73.5 μmol) were added, and the mixture was stirred for 72 h under N_2 atmosphere. The solvent was removed, and the crude product washed with methanol twice to give a yellow solid (2.22 g,

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84%); 1.66 g (2.3 mmol) of this material was dissolved in a THF (350 mL)/water (250 mL) mixture and concd. HCl (50.0 mL) was added. After 24 h, the extraction with dichloromethane furnished **5** (1.30 g, 89%): mp >305 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.02 (s, 2H), 7.94 (s, 2H), 7.91 (d, J = 8.3 Hz, 4H), 7.83 (d, J = 16.4 Hz, 2H), 7.72 (d, J = 8.1 Hz, 4H), 7.55 (d, J = 8.5 Hz, 4H), 7.45 (d, J = 8.5 Hz, 4H), 7.33 (d, J = 16.5 Hz, 2H), 1.37 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 152.5, 143.3, 137.2, 135.7, 131.5, 130.4, 129.5, 129.2, 129.1, 127.3, 125.8, 123.1, 120.0, 96.6, 86.9, 35.1, 31.3; IR (cm^{-1}) 2958, 2904, 2867, 1693, 1597, 1565, 1513, 1474, 1463, 1389, 1362, 1304, 1267, 1213, 1165, 1103, 1015, 958, 860, 828, 807, 788, 735.71, 652, 626, 559, 514; HRMS (EI) m/z calcd for $C_{48}H_{42}O_2$ [M]$^+$ 650.3184, found 650.3144.

General Procedure for Imine Formation of 5 with Amines. A reaction mixture of **5** (300 mg, 460.9 μmol) and the amine (1.8 mmol) was stirred in THF (20 mL) for 24 h at room temperature. Removal of solvent followed by suspension in methanol and centrifugation followed by washing with methanol furnished **6** as a yellow solid.

1,4-Bis(4-*tert*-butylphenylethynyl)-(*E*)-2,5-bis(4-((cyclopropylimino)methyl)styryl)benzene (6a): 93% yield (314 mg); mp >236 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.88 (s, 2H), 7.71 (d, J = 16.4 Hz, 2H), 7.68 (d, J = 8.2 Hz, 4H), 7.57 (d, J = 8.3 Hz, 4H), 7.54 (d, J = 8.6 Hz, 4H), 7.43 (d, J = 8.5 Hz, 4H), 7.25 (d, J = 16.4 Hz, 2H), 3.09−3.00 (m, 2H), 1.37 (s, 18H), 1.01−0.94 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 152.2, 139.2, 137.4, 136.2, 131.5, 130.2, 128.9, 128.1, 127.1, 126.8, 125.7, 122.7, 120.2, 96.2, 87.3, 42.3, 35.0, 31.3, 9.1; IR (cm^{-1}) 2959, 2865, 1599, 1507, 1301, 1170, 1103, 1012, 955, 884, 809, 564, 535; HRMS (ESI) m/z calcd for $C_{54}H_{53}N_2$ [M + H]$^+$ 729.4203, found 729.4213.

(*E*)-2,5-Bis(4-((benzylimino)methyl)styryl)-1,4-bis(4-*tert*-butylphenylethynyl)benzene (6b): 86% yield (330 mg); mp >190 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 2H), 7.92 (s, 2H), 7.81 (d, J = 8.2 Hz, 4H), 7.76 (d, J = 16.5 Hz, 2H), 7.63 (d, J = 8.3 Hz, 4H), 7.55 (d, J = 8.4 Hz, 4H), 7.43 (d, J = 8.5 Hz, 4H), 7.38−7.26 (m, 12H), 4.85 (s, 4H), 1.36 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 152.0, 139.7, 139.3, 135.6, 131.3, 131.3, 129.9, 128.8, 128.7, 128.5, 128.0, 127.0, 126.9, 126.9, 125.6, 122.6, 120.0, 96.1, 87.1, 65.1, 34.9, 31.2; IR (cm^{-1}) 3027, 2959, 2902, 2865, 2208, 1907, 1800, 1638, 1599, 1512, 1452, 1267, 1103, 1024, 957, 831, 730, 695, 559, 524; HRMS (EI) m/z calcd for $C_{62}H_{56}N_2$ [M]$^+$ 828.4444, found 828.4444.

1,4-Bis(4-*tert*-butylphenylethynyl)-(*E*)-2,5-bis(4-(((1-(*tert*-butoxycarbonyl)piperidin-4-yl)imino)methyl)styryl)benzene (6c): 87% yield (409 mg); mp >255 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 2H), 7.90 (s, 2H), 7.75 (d, J = 8.4 Hz, 4H), 7.74 (d, J = 16.2 Hz, 2H), 7.60 (d, J = 8.3 Hz, 4H), 7.54 (d, J = 8.5 Hz, 4H), 7.43 (d, J = 8.5 Hz, 4H), 7.28 (d, J = 16.3 Hz, 2H), 4.10 (d, J = 12.0 Hz, 4H), 3.40 (quin, J = 6.8 Hz, 2H), 3.01 (quin, J = 6.7 Hz, 4H), 1.75 (m, 8H), 1.49 (s, 18H), 1.36 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 155.1, 152.2, 139.8, 137.4, 135.9, 131.4, 130.1, 129.0, 128.8, 127.1, 127.1, 125.7, 122.7, 120.1, 96.2, 87.2, 79.6, 67.5, 35.0, 33.5, 33.4, 31.3, 28.4; IR (cm^{-1}) 2964, 2864, 2202, 1685, 1426, 1364, 1234, 1167, 832, 812, 563, 532; HRMS (ESI) m/z calcd for $C_{68}H_{79}N_4O_4$ [M + H]$^+$ 1015.6096, found 1015.6101.

1,4-Bis(4-*tert*-butylphenylethynyl)-(*E*)-2,5-bis(4-(((3-(dimethylamino)propyl)imino)methyl)styryl)benzene (6d): 82% yield (207 mg); mp >181 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.90 (s, 2H), 7.74 (d, J = 16.4 Hz, 2H), 7.74 (d, J = 8.3 Hz, 4H), 7.61 (d, J = 8.3 Hz, 4H), 7.54 (d, J = 8.5 Hz, 4H), 7.43 (d, J = 8.5 Hz, 4H), 7.28 (d, J = 16.3 Hz, 2H), 3.67 (t, J = 6.9 Hz, 4H), 2.38 (t, J = 7.4 Hz, 4H), 2.26 (s, 12H), 1.90 (quin, J = 7.3 Hz, 4H), 1.36 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 152.2, 139.6, 137.4, 136.0, 131.5, 130.1, 129.0, 128.7, 127.1, 125.7, 122.7, 120.1, 96.2, 87.2, 59.9, 57.7, 45.7, 35.0, 31.3, 29.1; IR (cm^{-1}) 2944, 2813, 2762, 1788, 1640, 1512, 1458, 1266, 1101, 955, 831, 809, 559. HRMS (ESI) m/z calcd for $C_{58}H_{67}N_4$ [M + H]$^+$ 819.5360, found 819.5369.

1,4-Bis(4-*tert*-butylphenylethynyl)-(*E*)-2,5-bis(4-(((2-hydroxyethyl)imino)methyl)styryl)benzene (6e): 92% yield (312 mg); mp >245 °C dec; ^{1}H NMR (300 MHz, THF-d_8) δ 8.29 (s, 2H), 8.00 (s, 2H), 7.80 (d, J = 16.5 Hz, 2H), 7.78 (d, J = 8.0 Hz, 4H), 7.66 (d, J = 8.2 Hz, 4H), 7.56 (d, J = 8.5 Hz, 4H), 7.48 (d, J = 8.5 Hz, 4H), 7.46 (d, J = 16.6 Hz, 2H), 3.78−3.65 (m, 8H),1.36 (s, 18H); ^{13}C NMR (75 MHz, THF-d_8) δ 161.9, 152.9, 140.4, 138.3, 137.5, 132.1, 131.3, 129.6, 129.4, 127.6, 127.2, 126.4, 123.5, 121.1, 96.9, 87.8, 65.1, 62.6, 35.5, 31.5; IR (cm^{-1}) 3241, 3030, 2954, 2867, 2328, 2210, 1642, 1599, 1506, 1062, 960, 831, 815, 559, 516; HRMS (ESI) m/z calcd for $C_{52}H_{53}N_2O_2$ [M + H]$^+$ 737.4102, found 737.4107.

1,4-Bis(4-*tert*-butylphenylethynyl)-(*E*)-2,5-bis(4-(((2-(dimethylamino)ethyl)imino)methyl)styryl)benzene (6f): 80% yield (291 mg); mp >140 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.89 (s, 2H), 7.74 (d, J = 8.4 Hz, 4H), 7.73 (d, J = 16.2 Hz, 2H), 7.59 (d, J = 8.3 Hz, 4H), 7.54 (d, J = 8.4 Hz, 4H), 7.43 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 16.3 Hz, 2H), 3.77 (t, J = 6.7 Hz, 4H), 2.66 (t, J = 7.0 Hz, 4H), 2.33 (s, 12H), 1.36 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 152.2, 139.7, 137.4, 135.8, 131.4, 130.1, 128.9, 128.7, 127.1, 125.7, 122.7, 120.1, 96.2, 87.2, 60.3, 60.2, 46.1, 35.0, 31.3. IR (cm^{-1}) 2955, 2904, 2862, 2767, 2204, 1692, 1363, 1166, 959, 831, 812, 559; HRMS (ESI) m/z calcd for $C_{56}H_{63}N_4$ [M + H]$^+$ 791.5047, found 791.5051.

1,4-Bis(4-*tert*-butylphenylethynyl)-(*E*)-2,5-bis(4-(((pyridin-2-ylmethyl)imino)methyl)styryl)benzene (6g): 75% yield (162 mg); mp >150 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, J = 4.2 Hz, 2H), 8.48 (s, 2H), 7.90 (s, 2H), 7.83 (d, J = 8.2 Hz, 4H), 7.75 (d, J = 16.5 Hz, 2H), 7.71−7.65 (m, 2H), 7.62 (d, J = 8.2 Hz, 4H), 7.55 (d, J = 8.4 Hz, 4H), 7.49−7.40 (m, 6H), 7.28 (d, J = 16.2 Hz, 2H), 7.22−7.16 (m, 2H), 4.98 (s, 4H), 1.36 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) 162.8, 159.5, 152.2, 149.4, 140.0, 136.8, 135.7, 134.3, 133.9, 131.5, 130.1, 129.0, 127.3, 127.1, 125.7, 122.8, 122.5, 122.2, 120.1, 96.3, 87.2, 67.1, 35.1, 31.4;. IR (cm^{-1}) 2958, 2903, 2865, 1693, 1597, 1266, 1103, 957, 831, 812, 750, 560, 524; HRMS (ESI) m/z calcd for $C_{60}H_{55}N_4$ [M + H]$^+$ 831.4421, found 831.4428.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of NMR spectra, spectroscopic data and titration plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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