# Novel two-photon-absorbing, 1,10-phenanthroline-containing $\pi$ -conjugated chromophores and their nickel(II) chelated complexes with quenched emissions

Qingdong Zheng, Guang S. He and Paras N. Prasad\*

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Novel 1,10-phenanthroline-containing  $\pi$ -conjugated chromophores with varied electron donors were synthesized and characterized together with their corresponding nickel(II) chelated complexes. The linear absorption maxima for these chromophores could be tuned from 357 to 415 nm by using different electron donors. The 1,10-phenanthroline-containing  $\pi$ -conjugated chromophores exhibit strong fluorescence in solutions upon one- or two-photon excitation. The fluorescence of these chromophores can be quenched or partially quenched by some metal ions due to an excellent metal ion chelating ability of the 1,10-phenanthroline backbone. The nickel(II) chelating complexes show quenched emission, both in dilute and concentrated solutions, compared to their metal ion-free chromophores. Their two-photon absorption (TPA) spectra are obtained using a newly developed multi-photon spectroscopic technique which utilizes a single strong femtosecond white-light continuum generation beam. The two-photon absorption spectra show that the TPA band for these compounds can be tuned by choosing different electron donors. The maximum TPA cross-section  $\sigma_2$  values for the three metal ion-free chromophores are variable from 0.58 to 2.26  $\times$  10<sup>-20</sup> cm<sup>4</sup> GW<sup>-1</sup> (±15%). The metal ion-free chromophore-containing dihexylamino groups (9c) has a larger TPA cross-section  $\sigma_2$  value compared to the chromophores containing alkyloxy groups or alkylthio groups. When the metal ion-free chromophores coordinate with the nickel(II) ion, the resulting complexes do not lose their excellent two-photonabsorbing ability. The nickel(II) chelated complexes display red-shifted two-photon absorption bands compared with their metal ion-free chromophores.

# 1. Introduction

Two-photon absorption (TPA) takes place when a molecule is excited from the ground state to an excited state by simultaneous absorption of two photons. Although this phenomenon was theoretically predicted by Maria Göppert-Mayer in 1931,<sup>1a</sup> and experimentally observed by Kaiser and Garrett in 1961,<sup>2</sup> few practical applications based on TPA had been considered until the advent of high power lasers and the availability of materials with large TPA. From the mid 1990s until now, increasing attention has been devoted to the TPAbased applications in photonic and biophotonic areas, such as optical data storage,<sup>3</sup> power limiting,<sup>4</sup> up-conversion lasing,<sup>5</sup> three-dimensional fluorescence imaging,<sup>6</sup> three-dimensional microfabrication,<sup>7</sup> pulse reshaping and stabilization,<sup>8</sup> and photodynamic therapy.9 At the same time, extensive efforts have been concentrated on the synthesis of chromophores with very large two-photon cross-section ( $\sigma_2$ ) values.<sup>10–14</sup> It has been observed by the Air Force Lab at Dayton that asymmetrical fluorene, bearing an electron donor and an electron acceptor, can display very large two-photon absorption.<sup>11</sup> Marder, Perry, and co-workers<sup>12</sup> discovered that symmetrical phenylene-vinylene oligomers, containing electron donors or electron acceptors, possess very large two-photon absorption. These molecular design strategies have proved to be useful in the preparation of novel materials with large twophoton absorption. Our group<sup>13</sup> and other groups<sup>14</sup> have developed some multi-branched chromophores with enhanced TPA. Most of the highly efficient two-photon-absorbing chromophores (*e.g.* AF 350 and AF  $389^{11}$ ) have strong fluorescence upon excitation by a strong laser beam. This feature is useful for some applications such as three-dimensional fluorescence imaging, two-photon pumped lasing and twophoton biosensing. However, it is undesirable for some other applications, such as optical power limiting, pulse reshaping and stabilization, and two-photon-induced photopolymerization. Therefore, there is a need to prepare chromophores with large TPA and quenched emission.

A control of the molecular geometry as well as the electronic structure, which are interconnected, is of crucial importance to optimize physical properties of chromophores. 1,10-Phenanthroline has a rigid framework and it possesses a superb ability to coordinate a large number of metal ions; the obtained metal complexes often show attractive chemical and physical properties (*e.g.* luminescence properties,<sup>15</sup> redox active behavior,<sup>16</sup> large optical nonlinearities<sup>17</sup>). A wide range of disubstituted 1,10-phenanthrolines are available which makes them attractive candidates for applications. Furthermore, their synthetic flexibility may allow one to tune the optical (absorption and emission) properties through

<sup>\*</sup>pnprasad@buffalo.edu

simple chemical modification of the ligands or metal ions. Some metal ions can be good quenchers because of photoninduced energy and charge transfer (CT). By incorporating two-photon-absorbing functional groups to the 1,10-phenanthroline backbone, followed by chelating to some metal ions, complexes with large TPA and quenched emission may be achieved. Despite their advantageous metal ion-binding properties, 1,10-phenanthroline-containing chromophores have rarely been employed for these purposes.<sup>18</sup> With the above considerations in mind, we designed a series of novel 1,10-phenanthroline-containing highly conjugated chromophores. The model structure for these chromophores is shown in Fig. 1. Long alkyl groups are incorporated into the model in order to increase their solubility in organic solvents. By changing the electron-donating ability of the terminal groups, chromophores with different absorption bands (linear and nonlinear) can be prepared. Dialkylamino, alkyloxy and alkylthio groups are chosen as electron donors. We describe in this paper the synthesis, linear and nonlinear optical properties of the 1,10-phenanthrolinecontaining  $\pi$ -conjugated chromophores, as well as investigation of metal ion effects on their linear and nonlinear optical properties.

# 2. Results and discussion

### Synthesis

The targeted compounds (9a, 9b, 9c, 10a, 10b and 10c) were synthesized according to Scheme 1. The basic strategies employed for synthesizing 1,10-phenanthroline-containing chromophores are based on Pd-catalyzed Suzuki crosscoupling reactions between 3,8-dibromo-1,10-phenanthroline and different boronic acids.19 The syntheses started with substituted benzaldehydes which were prepared by a number of different routes using known reactions.<sup>20-22</sup> 3,8-Dibromo-1,10-phenanthroline and (4-bromobenzyl)diethyl phosphonate was synthesized according to the literature procedure.<sup>23,24</sup> Substituted benzaldehydes and (4-bromobenzyl)diethyl phosphonate were coupled by the Horner-Emmons reaction in 78-90% yields.<sup>25</sup> The resulting bromides were converted to corresponding boronic acids in 21-75% yields by reaction of aryl lithium reagents with trimethyl borate at low temperature.<sup>26</sup> The Suzuki coupling reactions of aryl bromide (8a-c) with boronic acids were carried out under an argon atmosphere with  $Na_2CO_3$  as a base in toluene-water (2 : 1) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (52–70% yields). The nickel(II) chelating complexes were obtained in high yields from the reaction between 1,10-phenanthroline-containing chromophores (9a-c) and nickel(II) chloride (89-93%). FAB/MS supports the conclusions that the nickel(II) complexes (10a-c) were generated from the 2 : 1 complexation of compounds 9a-c with nickel(II).

### Linear absorption and emission properties

Linear absorption spectra for these compounds were recorded on a Shimadzu UV-3101 PC spectrophotometer using dilute solutions (10<sup>-5</sup> M in CHCl<sub>3</sub>). The linear absorption spectra are shown in Fig. 2. The electron-donating ability of donors is in the following order: dialkylamino > alkyloxy > alkylthio. Compound **9c** has the strongest donor, and displays a redshifted linear absorption  $\lambda_{max}$  (357 nm for **9a**, 376 nm for **9b** and 415 nm for **9c**), since a stronger electron donor will help to stabilize the charge-separated excited state of the molecule. All the metal ion chelated complexes possess red-shifted absorption bands compared to their corresponding metal ion-free chromophores.

One-photon excited fluorescence was measured in CHCl<sub>3</sub> dilute solutions  $(2 \times 10^{-6} \text{ M})$  by using a Jobin-Yvon Fluorog FL-311 spectrofluorometer. When these chromophores were excited at 375 nm, they underwent a one-photon excited emission process, with the emission maxima at wavelengths 445–541 nm and fluorescence quantum yields 7–20% (shown in Table 1, with reference to coumarin 152,  $\Phi_f = 0.21$  in ethanol).<sup>27</sup> As shown in Fig. 3, compounds **9a**, **9b** and **9c** have strong one-photon fluorescence. However, their metal-ion chelated complexes have negligible fluorescence (99% quenched emission). This quenched emission behavior is attributed to the fact that the normally emissive  $\pi$ - $\pi$ \* states decay rapidly *via* low-lying ligand field d–d or ring $\leftrightarrow$ metal charge transfer excited states ( $\pi$ -d) or (d- $\pi$ \*), as predicted by the extended Hückel theory.<sup>28</sup>

### **Two-photon fluorescence**

Fluorescence spectral measurements were obtained using a HoloSpec CCD-array spectrometer in conjunction with a fiber coupler head. All the chromophores have no linear absorption in the range of 700–1000 nm. However, when the concentrated solutions (0.02 M for **9b** and **9c**, 0.01 M for **9a**) of the chromophores were excited by a 775 nm laser beam (*ca.* 5  $\mu$ J, f = 20 cm focusing lens), strong fluorescence with colors changing from blue, to green, to yellow can be seen and detected (Fig. 4). In contrast, no visible or detectable fluorescence was found for the nickel(II) chelated complexes.

### **Ionochromic effects**

Since the 1,10-phenanthroline unit can be chelated to different metal ions, different optical properties would be expected for



 $R^1$ =H, OC<sub>6</sub>H<sub>13</sub>;  $R^2$ =S(C(CH<sub>3</sub>)<sub>3</sub>), OC<sub>6</sub>H<sub>13</sub>, N(C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>

Fig. 1 Targeted model for 1,10-phenanthroline-containing  $\pi$ -conjugated chromophores.



Scheme 1 Synthetic routes for the targeted chromophores.

various metal ion chelated complexes. For this reason, compound **9c** was chosen as an example to investigate the ionochromic effect for this type of chromophores. Upon addition of some metal ions to the chromophore solution, there was an instant change in linear absorption as well as in emission. The linear absorption and emission properties for **9c** solutions containing different metal ions are shown in Table 2. The metal ion chelated complexes would have d–d and CT bands; however, these bands are of low intensity and are masked by the intense  $\pi$ - $\pi$ \* absorption. Our results show that some other transition metal ions (Cu<sup>+</sup>, Fe<sup>3+</sup>) can also be used to quench the emission. The linear absorption and emission for the compound **9c** solution shifted when zinc(II), silver(I) and tin(II) were added to the solution. However, potassium ion addition has no influence on its absorption and emission

properties because there is no coordination between the ligand and the potassium ions.

# Degenerate two-photon absorption spectra

Nanosecond excitations are not sufficient for separating the contribution of excited-state absorption from that of instantaneous two-photon absorption. Therefore, femtosecond twophoton absorption spectra are required in order to study the molecular structure–property relationships. In the latter case, the excited-state absorption can be ignored due to the ultrashort laser pulse duration.

Degenerate TPA spectral measurements<sup>29</sup> for these compounds were accomplished by using a spectrally dispersed femtosecond white-light continuum generated from a  $2.5 \times 2.5$  cm



Fig. 2 Linear absorption spectra for compounds 9a-c and 10a-c.

right-angle quartz prism. The specially designed experimental set-up used for this study is illustrated in Fig. 5. The pump source for continuum generation is a focused ultra-short pulsed laser beam from a Ti:sapphire laser/amplifier system (model CPA-2010 from Clark-MXR). The pulse duration, wavelength, repetition rate and the pulse energy of the pump beam were ca. 160 fs, ca. 775 nm, 1 kHz, and 180 µJ, respectively. The generated white-light continuum beam was then collimated and passed through a dispersion prism made of SF10 glass. Such a spatially/spectrally dispersed whitelight beam was focused onto the central region of a 1 cm path-length quartz cuvette via an f = 10 cm lens. The quartz cuvette is filled with the chromophore solution. With this particular experimental set-up, different spectral components of the white-light continuum beam are spatially separated from each other and only degenerate two-photon absorption from the same spectral components could take place within the sample solution. A CCD array detector was used to record the spectral intensity distribution of the transmitted continuum beam at the sample position. As shown in Fig. 5, the positions for the T = 92% filter and the T = 1% filter can be exchanged. Thus when the 92% filter is put in front of the sample solution (the T = 1% filter being behind the sample solution), the two-photon absorption process takes place because the passing white light is of high intensity. At the same time, strong two-photon excited fluorescence can be easily seen if a fluorescing sample is chosen for the measurement. However, when the T = 1% filter is placed in

front of the sample solution (the T = 92% filter being behind the sample), there is only negligible or no TPA for the given sample (no two-photon excited fluorescence can be seen) since the intensity of the white light is 92-fold decreased. By comparing the two recorded continuum spectral profiles of the sample solution upon the two different position combinations of these two filters, attenuation of different spectral components due to degenerate TPA of the studied chromophore can be determined. This nonlinear attenuation of different spectral components provides important information on the relative TPA crosssection values as a function of the wavelength for each chromophore, which can be finally converted into the TPA spectrum on an absolute scale of absorption cross-section values, based on a standard calibration process at a single laser wavelength.

We also measured the TPA spectra for chloroform using the same conditions and found that there was no measurable absorption in the range of 500–1100 nm. The TPA  $\lambda^{(2)}_{max}$ , and the TPA cross-section values for compounds 9a-c and 10a-c are listed in Table 1. Fig. 6 shows the measured TPA crosssections as a function of wavelength for compounds 9a-c and 10a-c. The TPA bands for metal ion chelated complexes are red-shifted compared with their corresponding metal ion-free chromophores. The intrinsic maximum TPA cross-section values for 9a, 9b, 9c, 10a, 10b and 10c are  $\sigma_2 = 0.58, 0.61,$ 1.59, 2.21, 2.26 and 2.50  $\times 10^{-20}$  cm<sup>4</sup> GW<sup>-1</sup> (±15%). These values are comparable to or larger than that of some highly active two-photon-absorbing chromophores investigated in our lab.<sup>11,13</sup> The large TPA cross-section values found for these chromophores can be attributed to the planarity of the ground-state geometry for the model chromophores. The 1,10phenanthroline backbone provides a rigid center-core which would favor intramolecular charge transfer and thus help to enhance two-photon absorption.12b

Compounds 9a, 9b and 9c have the same  $\pi$ -conjugation length but differ in the terminal groups. It was observed that the TPA cross-section value increased by approximately 170% in going from compound 9a to compound 9c and by 160% in going from compound 9b to compound 9c. These results reaffirmed that the TPA cross-section value can be enhanced by using strong electron donors in which the amount of intramolecular charge transfer increased. With the increasing electron-donating ability of the terminal groups, the  $\lambda^{(2)}_{max}$ red-shifts follow the same sequence as their linear absorption,

**Table 1** Linear and nonlinear optical data for compounds 9a-c and  $10a-c^a$ 

Chromophores	Absorption $\lambda_{max}/nm$	Emission $\lambda_{max}/nm^b$	$\frac{\text{TPA}}{\lambda^{(2)}_{\text{max}}/\text{nm}}$	$10^{20}$ TPA cross-section $\sigma_{2_{max}}$ /cm <sup>4</sup> GW <sup>-1</sup>	TPA cross-section $\sigma'_{2_{max}}/GM^c$
9a	357	445 (7%)	696	0.58	165
10a	392	Quenched	760	2.21	578
9b	376	466 (14%)	758	0.61	160
10b	411	Quenched	789	2.26	569
9c	415	541 (20%)	788	1.59	401
10c	369	Quenched	839	2.50	592

<sup>*a*</sup> The concentration of the solution samples for linear absorption and emission is fixed at  $10^{-5}$  M in CHCl<sub>3</sub>; the concentrations of the solution samples for femtosecond degenerate WLC measurements are 0.01 M (for **9a** and **10a–c**) and 0.02 M (for **9b** and **9c**). Each solution sample was filtered through a 0.2 µm Gelman acrodisc CR filter. <sup>*b*</sup> Quantum yield in parentheses; quantum yield ( $\Phi_f$ ) at room temperature was determined with coumarin 152 ( $\Phi_f = 0.21$  in ethanol) as a reference, excited at 375 nm. <sup>*c*</sup> 1 GM = 1 × 10<sup>-50</sup> cm<sup>4</sup> sec photon<sup>-1</sup> molecule<sup>-1</sup>.



Fig. 3 One-photon excited fluorescence spectra for compounds 9a-c and 10a-c.



Fig. 4 Two-photon excited fluorescence spectra for compounds **9a–c**; no detectable fluorescence was found for compounds **10a–c** (same as the background).

**Table 2** Absorption and emission response of compound 9c upon chelating with metal ions in chloroform–methanol  $(10:1)^a$ 

Run	Metal ion	s $\lambda_{\rm max}/{\rm nm}$	$\lambda_{\rm Em}/{\rm nm}$	Emission
1	Cu <sup>+</sup>	368, 475 (shoulder)		Ouenched
2	$Sn^{2+}$	289, 394 (shoulder)	526	Strong
3	Fe <sup>3+</sup>	Overlap with FeCl <sub>3</sub>		Quenched
4	Ni <sup>2+</sup>	350, 446 (shoulder)		Quenched
5	$Zn^{2+}$	354, 451 (shoulder)	505	Weak
6	$K^+$	416	582	Strong
7	$Ag^+$	439, 340 (shoulder)	665	Weak
8	Ion-free	416	582	Strong
<sup>a</sup> The	following 1	metal salts were used: Cu	ICl, SnCl <sub>2</sub> ,	FeCl <sub>3</sub> , NiCl <sub>2</sub> ,

ZnCl<sub>2</sub>, KCl, AgNO<sub>3</sub>; the concentration of compound **9c** is  $10^{-5}$  M, and the concentration of metal ions is fixed at  $10^{-4}$  M.

*i.e.* **9a**:  $\lambda^{(1)}_{\text{max}} = 357 \text{ nm}, \lambda^{(2)}_{\text{max}} = 696 \text{ nm};$  **9b**:  $\lambda^{(1)}_{\text{max}} = 376 \text{ nm}, \lambda^{(2)}_{\text{max}} = 758 \text{ nm};$  **9c**:  $\lambda^{(1)}_{\text{max}} = 415 \text{ nm}, \lambda^{(2)}_{\text{max}} = 788 \text{ nm}.$  The tunability of the TPA absorption band would be very useful for the broad-band optical power limiting application.

When the metal-free chromophores coordinate with nickel(II), the magnitude of the TPA cross-section increased except for compound 9c. Considering the molecular weight difference between the nickel(II) chelated complexes and the metal-free chromophores, the TPA cross-section value for compound 10a is still approximately 90% larger than that for compound 9a, and the TPA cross-section value for compound 10b is approximately 85% larger than that for compound 9b. As mentioned above, the TPA cross-section value correlates with intramolecular charge transfer to the  $\pi$ -bridge. The nickel(II) chelated complexes have an extended  $\pi$ -bridge considering the  $\pi$ -electron contribution from the nickel(II) metal ion. Moreover, the metal ion favors the intramolecular charge transfer from the donors to the  $\pi$ -bridge. Thus, an increased intramolecular charge transfer may be expected in the nickel(II) chelated complexes which accounts for their enhanced two-photon absorption. However, there is an approximate 20% decrease in the TPA cross-section value when compound 9c is chelated with nickel(II). This decrease showed that nickel(II) coordination may not help to increase the amount of intramolecular charge transfer in this case since the dialkylamino group itself is a very strong electron-donating group, unlike the weak electron donors such as alkyloxy and alkylthio groups. This result showed that a balance between the electron donor and the electron acceptor linked through the conjugation bridge is necessary for the optimization of the TPA cross-section. The nickel(II) chelated complexes display red-shifted two-photon absorption bands compared with their metal ion-free chromophores.

# 3. Conclusions

We report the design and synthesis of novel 1,10-phenanthroline-containing  $\pi$ -conjugated chromophores as well as their corresponding nickel(II) chelated complexes. In the designed model chromophores, a tunable linear absorption and emission bands were achieved by tuning the electron-donating abilities of the terminal groups. The 1,10-phenanthrolinecontaining  $\pi$ -conjugated chromophores possess strong fluorescence in solutions upon one- or two-photon excitation. The



Fig. 5 Optical set-up for single femtosecond continuum beam-based degenerate two-photon absorption spectral measurement.



Fig. 6 Two-photon absorption spectra for compounds 9a-c and 10a-c.

fluorescence for the metal ion-free chromophores can be quenched or partially quenched by introducing metal ions, owing to their excellent metal-ion chelating ability. The nickel(II) chelated complexes show quenched emission, both in dilute and concentrated solutions compared with their metal ion-free compounds. This quenching of emission is attributed to the fact that the normally emissive  $\pi$ - $\pi$ \* states decay rapidly *via* low-lying ligand field d-d or ring $\leftrightarrow$ metal charge transfer excited states ( $\pi$ -d) or (d- $\pi$ \*, as predicted by the extended Hückel theory.<sup>28</sup> Their two-photon absorption spectra are obtained by utilizing the femtosecond whitelight continuum generation technique. The maximum TPA cross-section  $\sigma_2$  values are 0.58, 0.61, 1.59, 2.21, 2.26 and  $2.50 \times 10^{-20} \text{ cm}^4 \text{ GW}^{-1} (\pm 15\%)$  for compounds 9a, 9b, 9c, 10a, 10b and 10c. The two-photon absorption spectrum showed that the TPA maximum  $\lambda^{(2)}_{max}$  and the magnitude can be tuned by using different electron donors which would be very useful for broad-band optical power limiting. Compound 9c possesses the largest TPA cross-section value among the three metal ion-free compounds, because the strong amino donor helps to enhance the intramolecular charge transfer. The nickel(II) chelated complexes have red-shifted two-photon absorption bands compared with their metal-free chromophores. Metal chelated compounds 10a and 10b showed enhanced two-photon absorption cross-section values compared with their metal ion-free chromophores. However, there is an approximate 20% decrease in the TPA cross-section value when compound 9c is chelated with nickel(II).

# 4. Experimental

<sup>1</sup>H NMR spectra were run at either 300, 400, or 500 MHz in CDCl<sub>3</sub>. Mass spectral determinations were carried out at 70 eV. Elemental analysis was performed by Atlantic Microlab, Inc. Column chromatography was carried out on silica gel 60 (230–400 mesh). All chemicals are commercially available from Lancaster Synthesis or the Aldrich Chemical Co. and were used as received unless stated otherwise.

# 4-tert-Butylthiobenzaldehyde<sup>20</sup> (6a)

To a solution of *t*-butylthiol (22.5 g, 0.25 mol) in 80 ml of DMSO containing potassium carbonate (33.0 g, 0.24 mol), 4-fluorobenzaldehyde (30.0 g, 0.24 mol) was added and the mixture was heated at 100 °C for 3 h with stirring. After cooling, the reaction mixture was poured into water, and the mixture was extracted with diethyl ether. The extracts were dried by MgSO<sub>4</sub> and evaporated to dryness. Distillation of the residue gave 42.0 g 4-*tert*-butylthiobenzaldehyde (90% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  10.03 (s, 1H), 7.83 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 8.0 Hz), 1.34 (s, 9H).

# 3,4-Bis-hexyloxybenzaldehyde<sup>21</sup> (6b)

3,4-Dihydroxybenzaldehyde (2.1 g, 0.015 mol), K<sub>2</sub>CO<sub>3</sub> (4.0 g, 0.03 mol) and 1-iodohexane (6.4 g, 0.03 mol) were stirred in 100 ml of 1-butanol under reflux for 24 h. After cooling, the 1-butanol was removed by rotary evaporation. The residue was dissolved in 200 ml of diethyl ether and washed with water and brine. The solution was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed to yield 3.7 g 3,4-bis-hexyloxybenzal-dehyde (85%) as a dark solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.83 (s, 1H), 7.41 (m, 2H), 6.95 (d, 1H, J = 8.5 Hz), 4.07 (m, 4H), 1.85 (m, 4H), 1.48 (m, 4H), 1.35 (m, 8H), 0.91 (m, 6H).

# 4-Formyl-N,N-dihexylaniline<sup>22</sup> (6c)

Anhydrous DMF (8.8 g, 0.12 mol) was cooled in an ice-water bath, and then phosphorus oxychloride (4 ml, 0.04 mol) was added dropwise, with stirring, from a syringe placed through the rubber septum. A bright yellow Vilsmeier–Haack reagent was formed. *N*,*N*-Dihexylaniline (9.1 g, 0.035 mol) was added quickly to the Vilsmeier–Haack reagent. After stirring for 30 min, the mixture was heated at 90 °C for one night. Then the mixture was cooled and poured into an ice-water–sodium acetate solution with vigorous stirring. The product was extracted from water with diethyl ether. The organic portion was washed with a 5% K<sub>2</sub>CO<sub>3</sub> aqueous solution (100 ml) to remove any remaining acid in the diethyl ether and then dried over anhydrous MgSO<sub>4</sub>. The organic phase was dried over MgSO<sub>4</sub> and evaporated under vacuum before purification by chromatography on silica gel (ethyl acetate–petroleum = 1 : 2) to give a yellow oil (8.8 g, 87% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.69 (s, 1H), 7.69 (d, 2H, J = 8.8 Hz), 6.63 (d, 2H, J = 8.8 Hz), 3.34 (t, 4H, J = 6.4 Hz), 1.59 (m, 4H), 1.32 (m, 12H), 0.89 (t, 6H, J = 6.4 Hz).

# General procedure for Horner-Emmons reaction<sup>25</sup>

To (4-bromobenzyl)diethyl phosphonate (0.025 mol) in 100 ml of dry THF was added sodium *tert*-butoxide (0.05 mol). The reaction mixture was cooled to 0 °C in an ice bath. Benzaldehydes (0.02 mol) were added to the solution, the ice bath was removed and the mixture was stirred at room temperature for 12 h. The product was poured into 200 ml of water and then THF was removed. The crude product was either collected by filtration or extracted twice with  $CH_2Cl_2$  and dried over anhydrous MgSO<sub>4</sub> and evaporated to dryness.

# 4-Bromo-4'-tert-butylstilbene (7a)

White crystalline solid, yield 78%. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (m, 6H), 7.38 (d, 2H, J = 8.1 Hz), 7.07 (s, 2H), 1.30 (s, 9H). HRMS calc. for C<sub>18</sub>H<sub>19</sub>BrS: 348.0365. Found: 348.0372.

# 4-Bromo-3'4'-bis-hexyloxystilbene (7b)

White crystalline solid, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (d, 2H, J = 8.4 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.02 (m, 3H), 6.85 (d, 2H, J = 16.4 Hz), 4.03 (m, 4H), 1.84 (m, 4H), 1.48 (m, 4H), 1.34 (m, 8H), 0.91 (m, 6H). HRMS calc. for C<sub>26</sub>H<sub>35</sub>BrO<sub>2</sub>: 458.1815. Found: 458.1814.

### 4-Bromo-4'-(N,N-di-n-hexylamino)stilbene (7c)

Yellow crystalline solid, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.41(d, 2H, J = 8.8 Hz), 7.35 (d, 4H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.4 Hz), 6.99 (d, 1H, J = 16.0 Hz), 6.78 (d, 1H, J = 16.0 Hz), 6.61 (d, 2H, J = 8.8 Hz), 3.27 (t, 4H, J = 7.6 Hz), 1.56 (m, 4H), 1.32 (m, 12 H), 0.90 (t, 6H, J = 6.4 Hz). HRMS calc. for C<sub>26</sub>H<sub>36</sub>BrN: 441.2026. Found: 441.2021.

# General procedure for preparation of compounds 8a-c<sup>26</sup>

A solution of compound 7 (0.03 mol) in dry THF (100 ml) was cooled to -78 °C. To this solution n-BuLi (14.4 ml, 2.5 M in hexane, 0.036 mol) was added dropwise through a dropping funnel. The mixture was stirred at this temperature for 3 h before 7.8 g of trimethyl borate (0.075 mol) dissolved in 20 ml of dry THF was added in a dropwise manner. The solution was allowed to warm to room temperature. The reaction was

quenched with dilute HCl (20%, 50 ml). The product was extracted with chloroform and dried over  $Na_2SO_4$ . After filtration and removal of the solvent under vacuum, the product was passed through a silica gel column (CH<sub>2</sub>Cl<sub>2</sub>–MeOH = 10 : 1).

### 4-Boronic acid-4'-tert-butylstilbene (8a)

White solid, 75% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (d, 2H, J = 7.5 Hz), 7.67 (d, J = 7.5 Hz, 2H), 7.53 (d, 2H, J = 7.8 Hz), 7.48 (d, 2H, J = 7.8 Hz), 7.17 (d, 2H, J = 16.5 Hz), 1.30 (s, 9H).

### 4-Boronic-3'4'-bis-hexyloxystilbene (8b)

White solid, 40% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.22 (d, 2H, J = 7.8 Hz), 7.63 (d, 2H, J = 7.8 Hz), 7.19 (d, 1H, J = 16.2 Hz), 7.04 (d, 1H, J = 16.2 Hz), 7.11 (m, 2H), 6.88 (d, 1H, J = 8.1 Hz), 4.03 (m, 4H), 1.85 (m, 4H), 1.49 (m, 4H), 1.35 (m, 8H), 0.92 (m, 6H).

### 4-Boronic acid-4'-(N,N-di-n-hexylamino)stilbene (8c)

Light yellow crystalline solid, 21% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (2H, d, J = 8.0 Hz), 7.59 (d, 2H, J = 8.0 Hz), 7.43 (d, 2H, J = 8.0 Hz), 6.64 (d, 2H, J = 8.0 Hz), 7.18 (d, 1H, J = 16.5 Hz), 6.95 (d, 1H, J = 16.5 Hz), 3.30 (t, 4H, J = 6.4 Hz), 1.58 (m, 4H), 1.33 (m, 12H), 0.90 (t, 6H, J = 6.4 Hz). HRMS calc. for (M + H<sup>+</sup>): 408.3078. Found: 408.3074.

# General procedure for Suzuki coupling reactions<sup>19</sup>

To a solution of 3,8-dibromo-1,10-phenanthroline **2** (0.67 g, 2 mmol), in toluene (6 ml) and H<sub>2</sub>O (3 ml), the corresponding boronic acids **8a–c** (5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.10 g, 0.09 mmol) and Na<sub>2</sub>CO<sub>3</sub> (1.47 g, 10 mmol) were added. The mixture was heated to reflux under an argon atmosphere for 24 h. When the reaction was completed, 50 ml of water was added to quench the reaction. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The crude solid was purified by chromatography on silica gel, using CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>CN (10 : 1) as the eluent to give compounds **9a–c**.

# 3,8-Bis-{4-[2-(4-*tert*-butylsulfanylphenyl)vinyl]phenyl}-[1,10]phenanthroline (9a)

White crystalline solid, 70% yield. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.45 (d, 2H, J = 1.8 Hz), 8.36 (d, 2H, J = 1.8 Hz), 7.85 (s, 2H), 7.78 (d, 4H, J = 7.8 Hz), 7.71 (d, 4H, J = 7.8 Hz), 7.55 (d, 4H, J = 8.4 Hz), 7.51 (d, 4H, J = 8.4 Hz), 7.19 (s, 4H), 1.32 (s, 18H). HRMS calc. for C<sub>48</sub>H<sub>44</sub>N<sub>2</sub>S<sub>2</sub>: 712.2940. Found: 712.2954. Elemental analysis: calc. for C<sub>48</sub>H<sub>44</sub>N<sub>2</sub>S<sub>2</sub>: C, 80.86; H, 6.22; N, 3.93. Found: C, 81.09; H, 6.15; N, 3.94%.

### 3,8-Bis-{4-[2-(3,4-bis-hexyloxyphenyl)vinyl]phenyl}-[1,10]phenanthroline (9b)

Yellow crystalline solid, 52% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.48 (d, 2H, J = 3.0 Hz), 8.43 (d, 2H, J = 3.0 Hz), 7.90 (s, 2H), 7.80 (d, 2H, J = 8.4 Hz), 7.68 (2H, d, J = 8.0 Hz), 6.89 (d, 2H, J = 8.4 Hz), 7.14 (d, 2H, J = 16.0 Hz), 7.06 (d,

2H, J = 16.0 Hz), 4.09 (t, 4H, J = 6.8 Hz), 4.04 (t, 4H, J = 6.8 Hz), 1.85 (m, 8H), 1.40 (m, 8H), 1.35 (m, 16H), 0.92 (m, 12H). HRMS calc. for  $C_{64}H_{76}O_4N_2$ : 936.5800. Found: 936.5834. Elemental analysis: calc. for  $C_{64}H_{76}N_2O_4$ : C, 82.01; H, 8.17; N, 2.99. Found: C, 81.92; H, 8.21; N, 3.02%.

# 3,8-Bis-{4-[2-(*N*,*N*-dihexylaminophenyl)vinyl]phenyl}-[1,10]phenanthroline (9c)

Yellow crystalline solid, 56% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.46 (2H, d, J = 2.0 Hz), 8.38 (2H, d, J = 2.0 Hz), 7.85 (s, 2H), 7.75 (4H, d, J = 8.5 Hz), 7.63 (4H, d, J = 8.5 Hz), 7.42 (d, 4H, J = 9.0 Hz), 7.13 (2H, d, J = 16.5 Hz), 6.94 (2H, d, J = 16.5 Hz), 6.64 (4H, d, J = 9.0 Hz), 3.29 (8H, t, J = 7.5 Hz), 1.60 (8H, m), 1.33 (m, 24 H), 0.91 (12H, t, J = 7.0 Hz). HRMS calc. for C<sub>64</sub>H<sub>78</sub>N<sub>4</sub>: 902.6221. Found: 902.6250. Elemental analysis: calc. for C<sub>64</sub>H<sub>78</sub>N<sub>4</sub>: C, 85.09; H, 8.70; N, 6.20. Found: C, 84.59; H, 8.51; N, 6.24%.

# General procedure for preparation of compounds 10a-c

A 0.5 mmol portion of compound 9 and 0.25 mmol of NiCl<sub>2</sub>·6H<sub>2</sub>0 were dissolved in 25 ml dichloromethane and then stirred for 8 h under reflux. After cooling to room temperature, an aqueous solution (10 ml) of NaPF<sub>6</sub> (0.5 mmol) was added. Dichloromethane was removed and 50 ml of hexane was added; the desired complex was precipitated, filtered, washed with water and dried under vacuum.

# Ni(9a)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (10a)

Yellow powder, 89% yield. <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ ):  $\delta$  8.87 (4H, br), 8.49 (4H, br), 8.26 (4H, br), 7.74 (8H, br), 7.52–7.22 (24H, m) 6.94–6.73 (8H, m), 1.28 (36H, s). FAB (M – 2PF<sub>6</sub>): 1482.6 calc.; 1482.5 found. Elemental analysis: calc. for  $C_{96}H_{88}F_{12}N_4NiP_2S_4$ : C, 64.97; H, 5.00; N, 3.16. Found: C, 64.68; H, 5.35; N, 3.72%.

### Ni(9b)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (10b)

Dark yellow powder, 91% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.83(4H, br), 8.15 (4H, br), 7.67 (4H, br), 7.34 (4H, br), 7.02–6.59 (32H, br), 4.05 (16H, m), 1.89 (16H, m), 1.32–1.60 (48H, br). 0.89 (24H, t). FAB (M – 2PF<sub>6</sub>): 1931.8 calc.; 1931.1 found. Elemental analysis: calc. for C<sub>128</sub>H<sub>152</sub>F<sub>12</sub>N<sub>4</sub>NiO<sub>8</sub>P<sub>2</sub>: C, 69.15; H, 6.89; N, 2.52. Found: 69.30; H, 6.70; N, 2.62%.

### Ni(9c)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (10c)

Red powder, 93% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 (4H, br), 8.22 (4H, br), 8.07 (4H, br), 7.63 (8H, br), 7.46 (8H, br), 7.19 (8H, br), 6.78 (8H, br), 6.54 (8H, br), 3.30 (16H, d), 1.59 (16H, d), 1.32 (48H, d), 0.90 (24H, d). FAB (M - 2PF\_6): 1863.2 calc.; 1863.2 found. Elemental analysis: calc. for C<sub>128</sub>H<sub>156</sub>F<sub>12</sub>N<sub>8</sub>NiP<sub>2</sub>: C, 71.33; H, 7.30; N, 5.20. Found: C, 71.36; H, 7.20; N, 5.42%.

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Qingdong Zheng, Guang S. He and Paras N. Prasad\*

Department of Chemistry, Institute for Lasers, Photonics and Biophotonics, State University of New York at Buffalo, Buffalo NY, 14260, USA. E-mail: pnprasad@buffalo.edu; Fax: 1-716-6456945

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