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Fluorescent solvatochromism of bi-polar *N*,*N*-diphenylaminoaryl-substituted hexaazatriphenylenes, tetraazaphenanthrene, and quinoxalines

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Abstract

1,4,5,8,9,12-Hexaazatriphenylenes, 1,4,5,8-tetraazaphenanthrene, and quinoxalines, each with six, four, and two *N*,*N*-diphenylaminobiphenyl and *N*,*N*-diphenylaminophenyl groups, respectively, were prepared and their absorption and fluorescent spectral behaviors were investigated. These compounds showed strong fluorescent solvatochromism arising from the donor-acceptor nature of the π-electron-deficient aromatic core and π-electron-rich diphenylamino terminal groups.

Keywords: Hexaazatriphenylene; Tetraazaphenanthrene; Solvatochromism; *N*,*N*-diphenylamino

1. Introduction

Interaction between a guest dye and a host molecule is reflected in a color of the guest (solvatochrimism), and thus the color of the dye can be tuned by the nature of the host molecule in a wide range of wavelength, especially when the dye guest molecule is of intramolecular charge-transfer (ICT) nature [1]. 1,4,5,8,9,12-Hexaazatriphenylene (HAT) [2] and 1,4,5,8-tetraazaphenanthrene (TAP) having three and two electron-withdrawing pyrazine rings, respectively, are of interest as an electron-poor core structure of electron-transporting and hole-blocking functions [3]. Introduction of aromatic rings at the peripheral region of HAT and TAP makes the compounds emissive. Also, the rings on the neighboring positions were expected to disturb the planarity of the HAT and TAP rings, leading to the formation of amorphous thin film. The corresponding phenyl- and biphenyl-substituted HAT and TAP formed fluorescent thin films on vacuum deposition [4]. When electron-rich aromatic groups such as *N*,*N*-diphenylaminoaryl [5] groups are introduced on the positions, emissive HAT and TAP of bi-polar [5,6] and solvatochromic [7] nature are created. Thus, the emitting color can be tuned by the nature of the host molecule in a wide range of wavelength, when they are used as an emissive dopant [8].

In the present article, bi-polar HAT, TAP, and quinoxaline derivatives, each with six, four, and two *N*,*N*-diphenylaminobiphenyl and *N*,*N*-diphenylaminophenyl groups, respectively, were prepared and their spectral behaviors were investigated.

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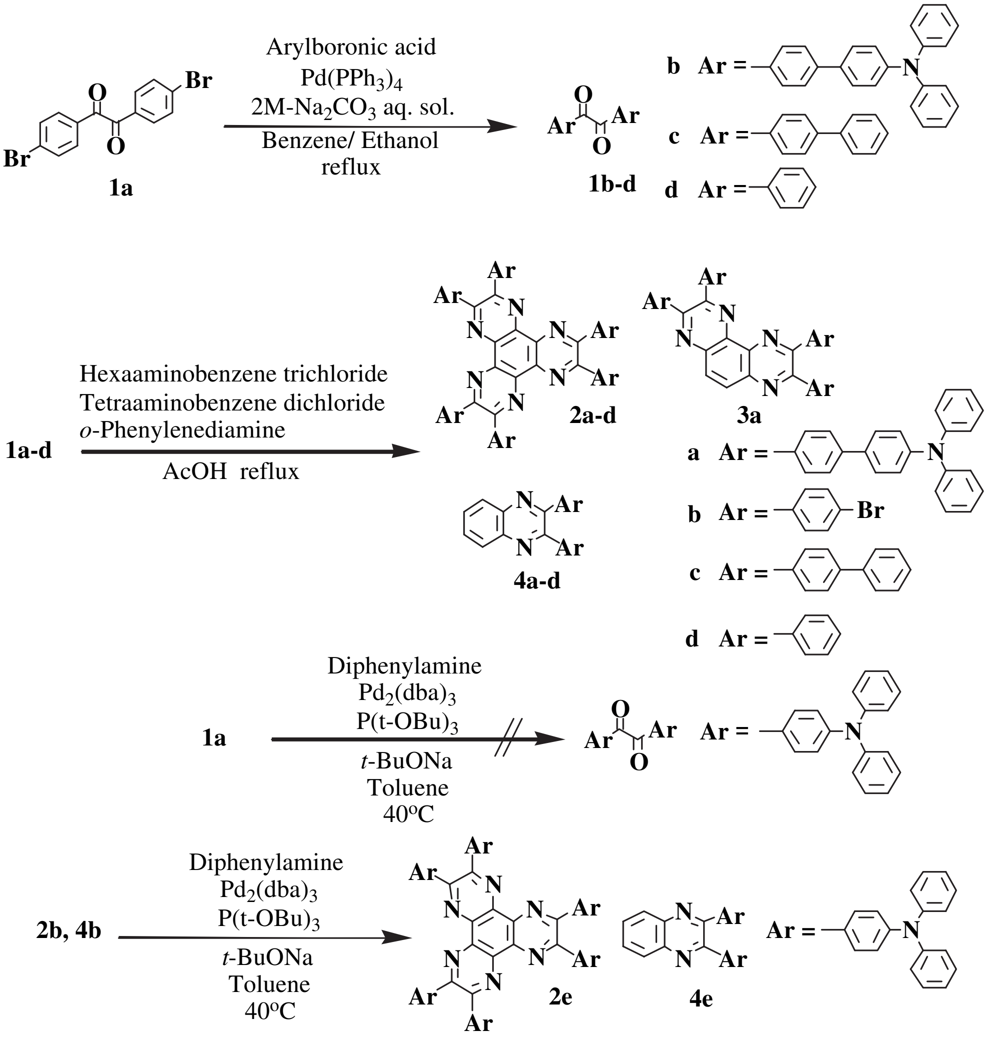
2. Results and discussion

2.1. Preparation

Compounds **2**, **3**, and **4** were prepared according to the methods reported previously (Scheme 1) [9]. Ethandiones **1b–c** were prepared by the coupling reactions of bis(*p*-bromophenyl)ethandione (**1a**) with the *p*-(*N*,*N*-diphenylamino)phenylboronic acid and phenylboronic acid, respectively. The condensation reaction of **1a–c** and benzil (**1d**) with aromatic benzene-1,2,3,4,5,6-hexaamine, -1,2,3,4-tetraamine, and -1,2-diamine in acetic acid gave the corresponding 1,4,5,8,9,12-hexaazatriphenylenes (**2a–d**), 1,4,5,8-tetraazaphenanthrene (**3**), and quinoxalines (**4a–b**). Pd-mediated coupling reaction of **1a** with diphenylamine leading to bis{*p*-(*N*,*N*-diphenylamino)phenyl}ethandione was unsuccessful. Compounds **2e** and **4e** were prepared by the coupling reaction of bromo derivatives **2b** and **4b** with diphenylamine.

2.2. Absorption spectra

The absorption spectral data of **2**, **3**, and **4** are summarized in Table 1. The λ_{max} of **2**, **3**, and **4** was independent upon the nature of the solvents such as toluene, THF, ethyl acetate, and dichloromethane. As the core size is expanded, λ_{max} appears in a longer wavelength region and the molar extinction coefficient (ε) is intensified, due to the increase in the number of chromophores. The *N*,*N*-diphenylamino group caused a red shift of λ_{max} in **2a** and **2e**, compared to the corresponding biphenyl and phenyl substituted derivative **2c** and **2d**. Interestingly, the shorter phenyl spacer is more effective for the red shift than the longer biphenyl spacer; the differences of λ_{max} are 27 nm between **2a** and **2c**, while 90 nm between **2e** and **2d**. These facts indicate the effective π–π conjugation between the core and peripheral *N*,*N*-diphenylaminophenyl function in **2e**, while the conjugation is disturbed between the two phenyl rings of the twisted biphenyl spacer of **2a**.



Scheme 1.

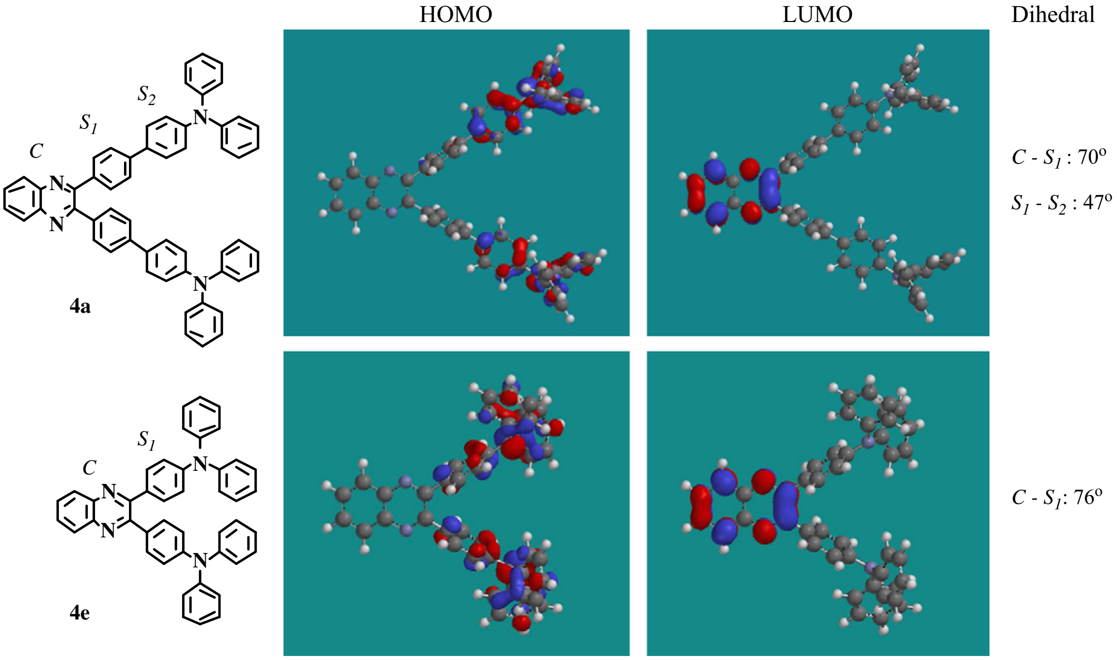
Table 1
Absorption properties of compound **2–4** in 10^{-5} M solution

Compound	Solvent	λ_{max} (nm)	ε	Compound	Solvent	λ_{max} (nm)	ε
2a	Toluene	417	129,000	**2e**	Toluene	453	98,000
	THF	412	135,000				
	EtOAc	415	123,000				
	CH_2Cl_2	416	120,000		CH_2Cl_2	454	92,000
2c	Toluene	392	68,000	**2d**	Toluene	366	21,000
	CH_2Cl_2	389	72,000		CH_2Cl_2	367	20,000
3	Toluene	403	83,000				
	THF	397	72,000				
	EtOAc	393	89,000				
	CH_2Cl_2	400	69,000				
4a	Toluene	376	83,000	**4e**	Toluene	403	21,000
	THF	374	72,000				
	EtOAc	372	89,000				
	CH_2Cl_2	372	69,000		CH_2Cl_2	403	20,000
4c	Toluene	360	20,000	**4d**	Toluene	342	9000
	CH_2Cl_2	357	18,000		CH_2Cl_2	343	10,000

Molecular structures of **4a** having biphenylene spacers and **4e** with phenyl spacers were calculated using MOPAC, PM3 method. Electron densities of the corresponding HOMO and LUMO molecular orbitals of **4a** and **4e** are shown in Fig. 1. In the HOMO orbital of **4a** and **4e**, electrons are localized in the diphenylamino group, and in the core in the LUMO orbitals. In compound **4e** having phenylene spacers, the HOMO orbital in the diphenylamino group is close to the central core. On the other hand, the diphenylamino group and the central core are separated by the long biphenylene spacers in compound **4a**. Electronic transitions are mostly $\pi-\pi^*$, originating from the diphenylaminophenyl group.

2.3. Fluorescent spectra

The fluorescent spectral data of **2**, **3**, and **4** in toluene, THF, ethyl acetate, and dichloromethane are shown in Table 2. Compounds **2a**, **2e**, **3**, **4a,** and **4e**, which have *N*,*N*-diphenylamino functions, are strongly fluorescent in solution and solid state. Their fluorescent maxima shifted to red, depending upon the core size and the length of the aromatic spacer. The emission maximum (λ_{FL}) of **2a**, **2e**, **3**, **4a**, and **4e** are remarkably dependent upon solvents. Longer biphenylene spacer in the *N*,*N*-diphenylaminoaryl groups caused larger red shift. Compound **2a** having the symmetric discotic structure



Structural optimization was carried out with SPARTAN '02.

Fig. 1. HOMO and LOMO molecular orbital of compounds of **4a** and **4e** by PM3 method.

Table 2
Fluorescent properties of compound **2–4** in 10^{-6} M solution

Compound	Solvent	λ_{FL} (nm)	ϕ_{FL}[a]	τ	Compound	Solvent	λ_{FL} (nm)	ϕ_{FL}[a]
2a	Toluene	501	0.96	1.64	**2e**	Toluene	502	0.95
	THF	584	0.75					
	EtOAc	580	0.42					
	CH_2Cl_2	624	0.27	5.27		CH_2Cl_2	563	0.75
2c	Toluene	438	0.43		**2d**	Toluene	419	0.01
	CH_2Cl_2	449	0.50			CH_2Cl_2	424	0.03
3	Toluene	491	0.99	1.72				
	THF	571	0.97					
	EtOAc	568	0.45					
	CH_2Cl_2	614	0.16	4.81				
4a	Toluene	472	0.85	1.54	**4e**	Toluene	477	0.68
	THF	534	0.87					
	EtOAc	536	0.47					
	CH_2Cl_2	592	0.11	2.06		CH_2Cl_2	556	0.39
4c	Toluene	419	<0.01		**4d**	Toluene		
	CH_2Cl_2	424	<0.01			CH_2Cl_2		

[a] Determined relative to fluorescein in ethanol (for **2a**, **2c**, **2e**, **3a**, and **4a**) and to quinine sulfate in 1 N-H_2SO_4 aq. sol. (for **2d** and **4c**).

showed large stoke shifts of 208–220 nm in the solvents mentioned above. The color of the fluorescence covers from green (480 nm) to red (630 nm) by utilizing **2**, **3**, and **4**. The quantum yields (ϕ_{FL}) are high in toluene and decrease with increase of solvent polarity. Lifetime of the fluorescence (τ) is composed of a single exponential function and is solvent-dependent.

On the other hand, the fluorescent spectra of **2c** and **2d** without *N*,*N*-diphenylaminoaryl groups are independent of the solvents (Table 2). Compounds **4c** and **4d** showed very weak fluorescence. These facts mentioned above show that in the excited state the discotic molecules **2a** and **2e,** as well as unsymmetric **3**, **4a**, and **4e**, have polar and planar structures with an effective intramolecular charge-transfer (ICT).

Bi-polar character of **2a** was disclosed by the measurement of cyclic voltammetry. Compound **2a** showed the reversible reduction–oxidation couple in CH_2Cl_2 (Fig. 2). Reduction of the HAT ring and oxidation of the triarylamino function occurred at the potential of −1.48 V and 0.88 V, respectively. The difference (2.36 eV) in the two potentials fits well to the HOMO–LUMO energy gap (2.46 eV) calculated from the absorption tail of the spectrum in CH_2Cl_2. Compounds **3** and **4a** have bi-polar character, but their reduction processes are irreversible.

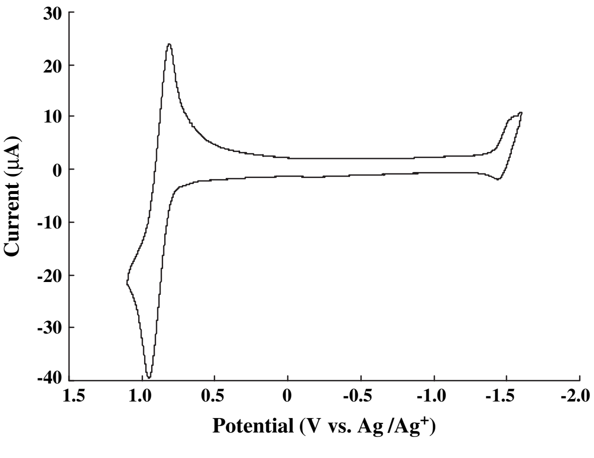


Fig. 2. Cyclic voltammogram of **2a** in CH_2Cl_2 solution.

3. Conclusion

Bipolar molecules **2a**, **2e**, **3**, **4a**, and **4c** are highly efficient fluorophores. As they showed large solvatochromism, their emitting color can be tuned by the nature of the host molecule from green (480 nm) to red (630 nm). These characteristics make these compounds potential emitters for organic-light-emitting diode OLED.

4. Experimental

4.1. General

All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus Fourier Transform Infrared Spectrophotometer as potassium bromide pellets. ^1H NMR spectra were determined in $CDCl_3$ with a JEOL GAX-270 or LA-400 spectrometer. Residual solvent protons were used as internal standard and chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (J) were reported in Hz. Elemental analyses were performed at the Elemental Analytical Center, Kyushu University. FAB–MS spectra were recorded with a JEOL JMS-01SG-2 mass spectrometer with *m*-nitrobenzyl alcohol as a matrix. Gel permeation chromatography (GPC) was performed with a Japan Analytical Industry Co. Ltd., LC-908 using a polystyrene JAIGEL-1H and -2H (20 × 600 mm) column eluting with chloroform/triethylamine (95:5, v/v) (2.5 mL/min). Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F_{245}). Column chromatography was carried out on silica gel (Wako C-300 or KANTO 60N). Absorption spectra were measured on a JASCO 220A spectrometer in a 1-cm width cell. Fluorescence spectra were measured on a HITACHI F4500 fluorescence spectrophotometer in a 1-cm width cell. Spectroscopic grade of dichloromethane, ethyl acetate, THF, and toluene were used and argon was bubbled in the solvent for 30 min before the measurement. Cyclic voltammetry was performed with a BAS 100B/W (CV 50W) electrochemical workstation, and a cell equipped with a glassy carbon as working electrode, Ag/Ag^+ as the reference electrode, and a platinum wire as counter electrode. Electrochemical measurements were performed in dichloromethane solution (5×10^{-4} M) containing 0.1 M tetra *n*-butylammonium hexfluorophosphate at room temperature.

*4.2. 2,3,6,7-Tetrakis[-4′-(diphenylamino)-1.1′-biphenyl-4-yl]-1,4,5,8-tetraazaphenanthrene (**3**)*

A mixture of tetraaminobenzene dihydrochloride (32 mg, 0.14 mmol) and bis[-4′-(diphenylamino)-1,1′-biphenyl-4-yl]ethanedion (200 mg, 0.29 mmol) in acetic acid (30 mL) was heated at the refluxing temperature for 24 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (50 mL × 3). The organic layer was washed with saturated aqueous sodium hydrogen carbonate solution (80 mL) and with brine (50 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was separated by silica gel column chromatography (Wakogel C-300); eluting with dichloromethane/*n*-hexane (2:1, v/v). The main fraction was evaporated in vacuo to dryness and the residue was purified by recrystallization from chloroform/*n*-hexane (1:1, v/v, 30 mL) to give **3** in 35% yield (150 mg, 0.10 mmol) as yellow powder: mp 204–206 °C; IR (cm^{-1}) 1590, 1493, 1368, 1327, 1280, 1100, 820; ^1H NMR (270 MHz) d 7.05 (t, $J = 7.2$ Hz, 8H, ArH), 7.12–7.16 (m, 16H, ArH), 7.24–7.31 (m, 24H, ArH), 7.54 (d, $J = 8.6$ Hz, 8H, ArH), 7.59–7.64 (m, 8H, ArH), 7.77 (d, $J = 8.6$ Hz, 4H, ArH), 7.87 (d, $J = 8.6$ Hz, 4H, ArH), 8.37 (s, 2H, ArH); FAB–MS *m/z* 1459 $[(M + H)^+]$, Anal. Calcd. for $C_{106}H_{74}N_8$: C, 87.21; H, 5.11; N, 7.68. Found: C, 86,70; H, 5.22; N, 7.68.

*4.3. 2,3-Bis[-4′-(diphenylamino)-1.1′-biphenyl-4-yl] quinoxaline (**4a**)*

A mixture of *o*-phenylenediamine (80 mg, 0.7 mmol) and bis[-4′-(diphenylamino)-1,1′-biphenyl-4-yl]ethanedion (500 mg, 0.7 mmol) in acetic acid (25 mL) was heated at the refluxing temperature for 24 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (50 mL × 3). The organic layer was washed with saturated aqueous sodium hydrogen carbonate solution (50 mL) and with brine (30 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was separated by silica gel column chromatography (Wakogel C-300); eluting with dichloromethane/*n*-hexane (1:1, v/v). The main fraction was evaporated in vacuo to dryness and the residue was purified by recrystallization from chloroform/*n*-hexane (1:1, v/v, 30 mL) to give **4a** in 81% yield (450 mg, 0.59 mmol) as yellow needles: mp 247–249 °C; IR (cm^{-1}) 1591, 1524, 1493, 1397, 1329, 1280, 1198, 1060, 1004, 978, 853, 821; ^1H NMR (270 MHz) d 7.04 (t, $J = 7.3$ Hz, 4H, ArH), 7.13 (d, $J = 8.7$ Hz, 12H, ArH), 7.27 (dd, $J = 7.3$, 8.7 Hz, 8H, ArH), 7.51 (d, $J = 8.7$ Hz, 4H, ArH), 7.57 (d, $J = 8.5$ Hz, 4H, ArH), 7.64 (d, $J = 8.5$ Hz, 4H, ArH), 7.78 (dd, $J = 3.4$, 6.4 Hz, 2H, ArH), 8.19 (dd, $J = 3.4$, 6.4 Hz, 2H, ArH); FAB–MS *m/z* 769 $[(M + H)^+]$; Anal. Calcd. for $C_{56}H_{40}N_4$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.20; H, 5.30; N, 7.33.

*4.4. 2,3-Bis(p-bromophenyl)quinoxaline (**4b**)*

A mixture of *o*-phenylenediamine (580 mg, 5.43 mmol) and di(*p*-bromophenyl)ethandione (2.00 mg, 5.43 mmol) in acetic acid (30 mL) was heated at reflux for 2 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (30 mL × 5). The organic layer was washed with saturated aqueous sodium hydrogen carbonate solution (100 mL) and brine (50 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was separated by silica gel column chromatography (Wako gel C-300); eluting with dichloromethane and purified by recrystallization from dichloromethane/*n*-hexane (1:1, v/v, 30 mL) to give **3c** in 86% yield (2.06 g, 4.68 mmol) as colorless needles: mp 195–197 °C; IR (cm^{-1}) 1586, 1556, 1489, 1391, 1343, 1221, 1070, 1048, 1010, 976, 841, 828; ^1H NMR (395 MHz) 7.41 (d, $J = 8.5$ Hz, 4H, ArH), 7.51 (d, $J = 8.5$ Hz, 4H, ArH), 7.80 (dd, $J = 3.4$, 6.4 Hz, 2H, ArH), 8.16 (d, $J = 3.4$, 6.4 Hz, 2H, ArH); FAB–MS *m/z* 439, 441, 443 $[(M + H)^+]$; Anal. Calcd. for $C_{20}H_{12}N_2Br_2$: C, 54.58; H, 2.75; N, 6.36. Found: C, 54.47; H, 2.87; N, 6.09.

*4.5. 2,3-Bis(4-diphenylaminophenyl) quinoxaline (**4e**)*

A mixture of 2,3-bis-(4-bromophenyl)quinoxaline (**3c**) (300 mg, 0.68 mmol), diphenylamine (576 mg, 3.41 mmol), tris(dibenzylideneacetone)dipalladium (312 mg, 0.34 mmol), 0.5 M tri(*tert*-buthyl)phosphine in toluene solution (684 mL, 0.34 mmol), sodium *tert*-buthoxide (983 mg, 10.23 mmol) in toluene (30 mL) was heated at 40 °C for 12 h under an argon atmosphere. After the reaction mixture was poured into water and extracted with dichloromethane (30 mL × 5) the organic layer was washed with brine (50 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was separated by silica gel column chromatography (Wakogel C-300); eluting with dichloromethane and purified by recrystallization from dichloromethane/*n*-hexane (1:1, v/v, 30 mL) to give **4b** in 86% yield (361 mg, 0.59 mmol) as yellow needles: mp 220–222 °C; IR (KBr, cm^{-1}) 1590, 1493, 1327, 1273, 1176, 1054, 977, 837; ^{1}H NMR (270 MHz) 7.04 (d, $J = 8.5$ Hz, 4H, ArH), 7.06 (t, $J = 7.3$ Hz, 4H, ArH), 7.13 (d, $J = 7.3$ Hz, 8H, ArH), 7.27 (t, $J = 7.3$ Hz, 8H, ArH), 7.44 (d, $J = 8.5$ Hz, 4H, ArH), 7.73 (dd, $J = 3.3$, 6.4 Hz, 2H, ArH) 8.13 (dd, $J = 3.3$, 6.4 Hz, 2H, ArH); FAB–MS *m*/*z* 617 [$(\mathrm{M + H})^+$]; Anal. Calcd. for $C_{44}H_{32}N_4$: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.67; H, 5.29; N, 9.03.

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