

SUPPORTING INFORMATION

Facile Synthesis and Characterization of Naphthidines as a New Class of Highly Nonplanar Electron Donors Giving Robust Radical Cations

Christophe Desmarets,[†] Benoît Champagne,[‡] Alain Walcarius,^{§} Christine Bellouard,[¥] Rafik Omar-Amrani,[†] Abdelaziz Ahajji,[□] Yves Fort[†] and Raphaël Schneider^{*†}*

[†] Synthèse Organométallique et Réactivité, UMR 7565, Faculté des Sciences, BP 239, 54506 Vandoeuvre les Nancy, France

[§] Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR 7564, CNRS – Université Henri Poincaré Nancy I, 405 rue de Vandoeuvre, 54600 Villers-les-Nancy, France

[‡] Laboratoire de Chimie Théorique Appliquée, FUNDP, Rue de Bruxelles 61, 5000 Namur, Belgium

[¥] Laboratoire de Physique des Matériaux, UMR 7556, Faculté des Sciences, BP 239, 54506 Vandoeuvre les Nancy, France

[□] Laboratoire d'Etudes et de Recherche sur le Matériau Bois, UMR 1093, Faculté des Sciences, BP 239, 54506 Vandoeuvre les Nancy, France

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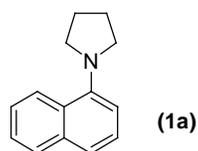
Experimental Section

All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen. GC and GC-MS analyses were conducted with an Optima 5 column. All quantifications of reaction constituents were achieved by gas chromatography using a known quantity of decane as reference standard. Melting points were taken on a Tottoli apparatus and were uncorrected. The ^1H , ^{19}F and ^{13}C NMR spectra were recorded at 400.13, 235.0 and 100.40 MHz using CDCl_3 as solvent. All ^{13}C , and ^{19}F NMR spectra are proton decoupled. IR spectra were recorded using NaCl cells or mixture of compounds/KBr. Compounds previously described were characterized by ^1H and ^{13}C NMR and their purity was confirmed by GC/MS analysis. All new compounds were fully characterized by ^1H and ^{13}C NMR, IR and elemental analysis.

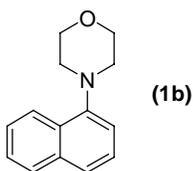
THF and dioxane were distilled under nitrogen from sodium benzophenone ketyl. *Tert*-butanol was distilled from sodium before use. CH_2Cl_2 was distilled under nitrogen from CaH_2 . Sodium hydride (65% in mineral oil) was used after two washings with THF under nitrogen. Aryl halides were purchased from commercial sources and were used without further purification. Amines were purchased from commercial sources and were distilled or passed through alumina before use. Nickel(II) acetylacetonate and titanium (IV) chloride were used as received.

General Procedure for the Amination of 1-chloronaphthalene using Secondary Cyclic Amines. A

50 mL Schlenk tube was loaded with degreased NaH (16 mmol), Ni(acac)₂ (0.5 mmol, 5 mol%), SIPr.HCl (0.5 mmol, 5 mol%) and 6 mL of dioxane and the mixture was heated to reflux. A solution of *t*-BuOH (15 mmol) in 3 mL of dioxane was then added dropwise followed by the amine (15 mmol), and the mixture was further stirred for ½ h. A solution of 1-chloronaphthalene (10 mmol) in 3 mL dioxane was then added and the reaction was monitored by GC. After complete consumption of the aryl chloride, the mixture was cooled to room temperature and adsorbed onto silica gel. The crude reaction mixture was purified by silica gel chromatography.



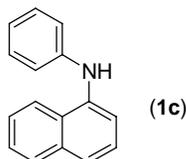
1-(1-Naphthyl)pyrrolidine¹ (1a). The general procedure was used to couple 1-chloronaphthalene and pyrrolidine. The title compound was isolated as a yellow oil (85%). ¹H NMR (400 MHz, CDCl₃) δ 7.76-7.74 (m, 2H), 7.67-7.65 (m, 1H), 7.53-7.49 (m, 1H), 7.44-7.38 (m, 2H), 6.90 (d, *J* = 7.20 Hz, 1H), 3.30-3.28 (m, 4H), 1.94-1.92 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 130.2, 128.1, 127.1, 126.5, 125.6, 124.1, 121.2, 111.3, 52.5, 24.5. MS : *m/z* = 197.



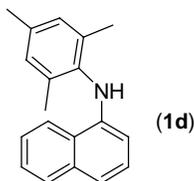
4-(4-Naphthyl)morpholine² (1b). The general procedure was used to couple 1-chloronaphthalene and morpholine. The title compound was isolated as a yellow oil (86%). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.77 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.52-7.29 (m, 4H), 6.98 (d, *J* = 7.6 Hz, 1H), 3.92-3.87 (m, 4H), 3.03-2.98 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 134.6, 128.3, 125.6, 125.2,

123.6, 123.2, 114.4, 67.2, 53.3. MS : $m/z = 213$.

General Procedure for the Amination of 1-chloronaphthalene using Anilines. A 50 mL Schlenk tube was loaded with degassed NaH (16 mmol), Ni(acac)₂ (0.5 mmol, 5 mol%), SIPr.HCl (1 mmol, 10 mol%) and 6 mL of dioxane, and the mixture was heated to reflux. A solution of *t*-BuOH (15 mmol) in 3 mL of dioxane was then added dropwise, and the mixture was further stirred for ½ h. A solution of 1-chloronaphthalene (10 mmol) and the aromatic amine (15 mmol) in 5 mL dioxane was then added dropwise and the reaction was monitored by GC. After complete consumption of the aryl chloride, the mixture was cooled to room temperature and adsorbed onto silica gel. The crude reaction mixture was purified by silica gel chromatography.

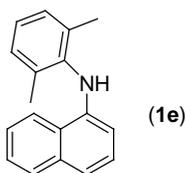


***N*-Phenyl-1-naphthalenamine³ (1c).** The general procedure was used to couple 1-chloronaphthalene and aniline. The title compound was isolated as a yellow oil (87%). IR (NaCl, cm⁻¹) : ν_{NH} 3386. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (dd, *J* = 5.6, 1.6 Hz, 1H), 7.53-7.49 (m, 1H), 7.42-7.40 (m, 1H), 7.34-7.21 (m, 1H), 7.02 (dd, *J* = 6.4, 1.6 Hz, 2H), 6.96-6.92 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 141.5, 129.4, 129.3, 126.1, 126.0, 125.6, 122.9, 121.8, 120.5, 118.2, 117.3, 115.8. MS : *m/z* = 219.

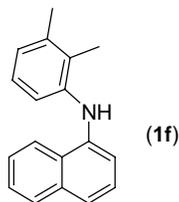


***N*-(2,4,6-Trimethylphenyl)-1-naphthalenamine⁴ (1d).** The general procedure was used to couple 1-chloronaphthalene and 2,4,6-trimethylaniline. The title compound was isolated as a red solid (82%). Mp

= 62°C. IR (KBr, cm^{-1}) : ν_{NH} 3389. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (dd, $J = 6.2, 3.4$ Hz, 1H), 7.83 (dd, $J = 6.2, 3.4$ Hz, 1H), 7.49-7.45 (m, 2H), 7.28-7.13 (m, 2H), 6.96 (s, 2H), 6.18 (dd, $J = 7.6, 1.0$ Hz, 1H), 2.32 (s, 3H); 2.18 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 135.9, 135.2, 135.1, 129.3, 128.6, 126.5, 125.7, 124.8, 120.2, 118.3, 115.9, 106.7, 20.9, 20.9. MS : $m/z = 261$.

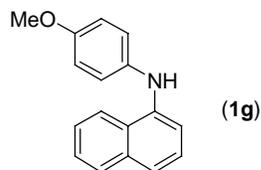


***N*-(2,6-Dimethylphenyl)-1-naphthalenamine⁴ (1e).** The general procedure was used to couple 1-chloronaphthalene and 2,6-dimethylaniline. The title compound was isolated as a brown solid (65%). Mp = 124°C. IR (KBr, cm^{-1}) : ν_{NH} 3389. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (dd, $J = 6.8, 2.0$ Hz, 1H), 7.83 (dd, $J = 6.8, 2.0$ Hz, 1H), 7.54-7.48 (m, 2H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.22-7.09 (m, 4H), 6.22 (d, $J = 7.6$ Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 138.7, 135.1, 134.5, 128.9, 128.8, 128.7, 128.6, 126.4, 125.8, 125.5, 125.0, 124.0, 120.3, 118.8, 107.3, 18.1. MS : $m/z = 247$.

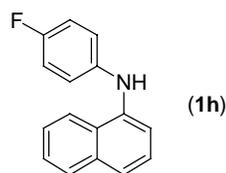


***N*-(2,3-Dimethylphenyl)-1-naphthalenamine (1f).** The general procedure was used to couple 1-chloronaphthalene and 2,3-dimethylaniline. The title compound was isolated as a red solid (83%). Mp = 58°C. IR (KBr, cm^{-1}) : ν_{NH} 3361. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, $J = 6.8, 2.4$ Hz, 1H), 7.82 (dd, $J = 6.8, 2.4$ Hz, 1H), 7.47-7.42 (m, 3H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.19-6.98 (m, 1H), 6.89-6.84 (m, 3H), 5.75 (s, 1H, NH), 2.33 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.0, 140.5, 137.7, 134.6, 128.5, 126.3, 126.2, 126.0, 125.9, 125.3, 124.3, 121.3, 121.2, 118.6, 113.3, 24.2, 20.6. MS : m/z

= 247. Anal. Calcd. for C₁₈H₁₇N : C, 87.41, H, 6.93, N, 5.66. Found : C, 87.53, H, 6.63, N, 5.84.

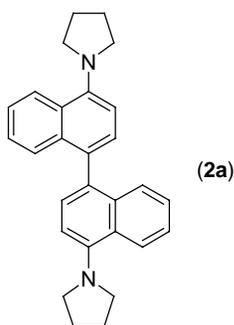


***N*-(4-Methoxyphenyl)-1-naphthalenamine⁵ (1g).** The general procedure was used to couple 1-chloronaphthalene and *p*-anisidine. The title compound was isolated as a red solid (82%). Mp = 58°C. IR (KBr, cm⁻¹) : ν_{NH} 3376. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.83 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.50-7.41 (m, 3H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H); 7.05 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.52 (s, 1H, NH), 3.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.1, 140.8, 136.8, 134.6, 128.5, 126.1, 126.0, 125.3, 121.8, 121.0, 120.9, 114.7, 111.7, 55.6. MS : *m/z* = 261.

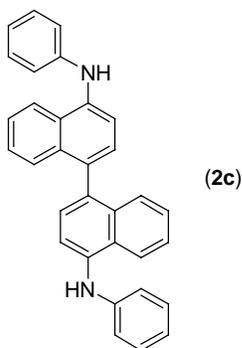


***N*-(4-Fluorophenyl)-1-naphthalenamine⁶ (1h).** The general procedure was used to couple 1-chloronaphthalene and 4-fluoroaniline. The title compound was isolated as a brown oil (76%). IR (NaCl, cm⁻¹) : ν_{NH} 3388. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.85 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.52-7.45 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33-7.21 (m, 1H), 6.96-6.94 (m, 4H), 5.84 (s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 157.7 (d, *J*_{C-F} = 239.5 Hz), 140.3, 139.5, 134.5, 128.4, 126.85, 126.0, 125.9, 125.4, 122.2, 121.4, 119.7 (d, *J*_{C-F} = 7.6 Hz), 115.6 (d, *J*_{C-F} = 22.5 Hz), 114.0; ¹⁹F NMR (235 MHz, CDCl₃) δ -37.55. MS : *m/z* = 233.

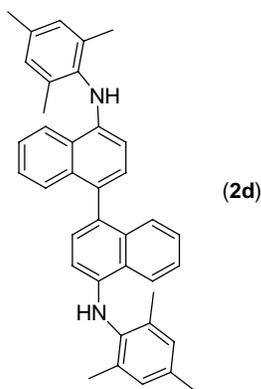
General Procedure for the TiCl₄-mediated Oxidative Coupling of Naphthylamines 1. A solution of naphthylamine **1** (5 mmol) in anhydrous CH₂Cl₂ (5 mL) was chilled to -5°C under nitrogen. TiCl₄ (1.7 mL of 1:1 solution of TiCl₄/CH₂Cl₂, 7.7 mmol) was added dropwise for 5 min. The reaction mixture was stirred at -5°C for 1 h and stirred further at 0°C for 8 h. A saturated K₂CO₃ solution (10 mL) was then added and the mixture was stirred for 0.5 h at 0°C. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The organic layers were combined, washed with brine solution (5 mL), dried over MgSO₄ and concentrated. The crude reaction mixture was purified by silica gel chromatography.



1,1'-Binaphthyl-4,4'-bis-pyrrolidine (2a). The general procedure was used to couple 1-(1-naphthyl)pyrrolidine **1a**. The title compound was isolated as a yellow solid (76%). Mp = 177°C. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.3 Hz, 2H), 7.42-7.33 (m, 6H), 7.24-7.20 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 3.42 (m, 4H), 2.05 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 134.4, 132.1, 128.2, 128.1, 127.1, 125.4, 124.7, 124.1, 111.2, 52.8, 24.8. Anal. Calcd. for C₂₈H₂₈N₂: C, 85.67, H, 7.19, N, 7.14. Found: C, 85.59, H, 6.95, N, 7.46.

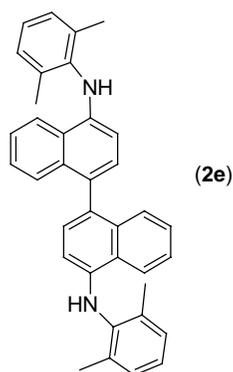


***N,N'*-Diphenyl-(1,1'-binaphthyl)-4,4'-diamine⁷ (2c).** The general procedure was used to couple *N*-phenyl-1-naphthalenamine **1c**. The title compound was isolated as a brown solid (59%). Mp = 167°C. IR (KBr, cm⁻¹) : ν_{NH} 3406. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.48-7.32 (m, 8H), 7.25-7.13 (m, 10H), 6.83 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 144.1, 138.1, 133.0, 131.3, 128.1, 127.2, 126.5, 125.9, 124.8, 123.9, 121.8, 118.8, 116.4, 113.3.

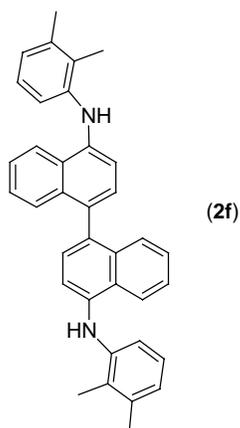


***N,N'*-Bis(2,4,6-trimethylphenyl)-(1,1'-binaphthyl)-4,4'-diamine (2d).** The general procedure was used to couple *N*-(2,4,6-trimethylphenyl)-1-naphthalenamine **1d**. The title compound was isolated as a brown solid (63%). Mp = 284°C. IR (KBr, cm⁻¹) : ν_{NH} 3404. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.51-7.48 (m, 4H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.20-7.18 (m, 2H), 7.03-7.01 (m, 4H), 6.29 (d, *J* = 8.4 Hz, 2H), 2.33 (s, 6H), 2.24 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 136.1, 135.1, 135.0,

134.2, 129.3, 129.2, 128.9, 127.6, 125.5, 124.6, 123.8, 120.3, 106.7, 20.9, 18.2. Anal. Calcd. for $C_{38}H_{36}N_2$: C, 90.13, H, 7.18, N, 2.70. Found: C, 90.27, H, 7.29, N, 2.70.

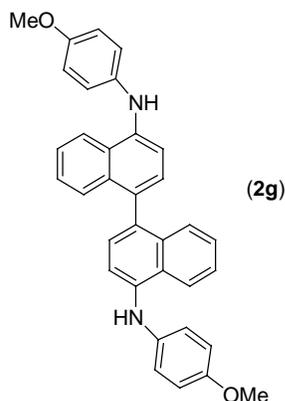


***N,N'*-Bis(2,6-dimethylphenyl)-(1,1'-binaphthyl)-4,4'-diamine (2e)**. The general procedure was used to couple *N*-(2,6-dimethyl)-1-naphthalenamine **1e**. The title compound was isolated as a brown solid (65%). Mp = 274°C. IR (KBr, cm^{-1}): ν_{NH} 3400. 1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, $J = 8.4$ Hz, 2H), 7.53-7.48 (m, 4H), 7.31 (t, $J = 8.0$ Hz, 2H), 7.23-7.17 (m, 6H), 7.13-7.09 (m, 2H), 6.32 (d, $J = 8.0$ Hz, 2H), 5.70 (s, 2H, NH), 2.28 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 140.6, 138.8, 135.0, 134.1, 129.5, 128.7, 128.6, 127.5, 125.5, 125.3, 124.7, 124.0, 120.5, 107.1, 14.1. Anal. Calcd. for $C_{36}H_{32}N_2$: C, 90.39, H, 6.76, N, 2.85. Found: C, 90.21, H, 6.83, N, 2.96.

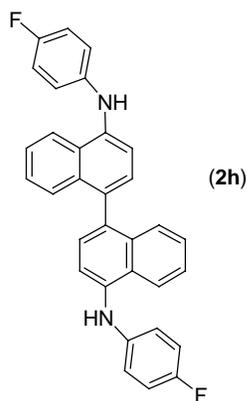


***N,N'*-Bis(2,3-dimethylphenyl)-(1,1'-binaphthyl)-4,4'-diamine (2f)**. The general procedure was used to couple *N*-(2,3-dimethyl)-1-naphthalenamine **1f**. The title compound was isolated as a yellow solid

(56%). Mp = 279°C. IR (KBr, cm^{-1}) : ν_{NH} 3372. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.33-7.25 (m, 4H), 7.00-6.95 (m, 8H), 6.90 (d, $J = 7.2$ Hz, 2H), 2.35 (s, 6H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.1, 140.2, 137.8, 134.2, 131.9, 128.5, 127.9, 127.5, 126.4, 126.2, 126.1, 125.9, 125.2, 124.4, 124.3, 123.5, 121.4, 118.8, 118.75, 112.9, 20.7, 13.7. Anal. Calcd. for $\text{C}_{36}\text{H}_{32}\text{N}_2$: C, 90.39, H, 6.76, N, 2.85. Found : C, 90.46, H, 6.85, N, 2.69.



***N,N'*-Bis(4-methoxyphenyl)-(1,1'-binaphthyl)-4,4'-diamine (2g)**. The general procedure was used to couple *N*-(4-methoxyphenyl)-1-naphthalenamine **1g**. The title compound was isolated as a brown solid (75%). Mp = 193°C. IR (KBr, cm^{-1}) : ν_{NH} 3372. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.6$ Hz, 2H), 7.49-7.43 (m, 4H), 7.33-7.27 (m, 4H), 7.20-7.18 (m, 2H), 7.13 (d, $J = 8.4$ Hz, 4H), 6.91 (d, $J = 8.4$ Hz, 4H); 3.81 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.1, 140.5, 136.8, 134.1, 131.5, 128.4, 127.5, 125.9, 125.8, 125.2, 122.0, 121.1, 114.9, 111.2, 55.6. Anal. Calcd. for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_2$: C, 84.82, H, 5.90, N, 2.83, O, 6.46. Found : C, 84.96, H, 5.78, N, 2.76.



***N,N'*-Bis(4-fluorophenyl)-(1,1'-binaphthyl)-4,4'-diamine (2h)**. The general procedure was used to couple *N*-(4-fluorophenyl)-1-naphthalenamine **1h**. The title compound was isolated as a brown oil (52%). IR (NaCl, cm^{-1}) : ν_{NH} 3389. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.49-7.45 (m, 4H), 7.34-7.29 (m, 6H), 7.04-6.98 (m, 6H), 6.16-6.04 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6 (d, $J_{\text{C-F}} = 239.5$ Hz), 140.4, 139.4, 134.1, 132.7, 128.7, 127.3, 126.1, 125.4, 121.5, 120.1 (d, $J_{\text{C-F}} = 13.0$ Hz), 116.0 (d, $J_{\text{C-F}} = 22.9$ Hz), 113.5; ^{19}F NMR (235 MHz, CDCl_3) δ -37.34. Anal. Calcd. for $\text{C}_{32}\text{H}_{22}\text{F}_2\text{N}_2$: C, 84.06, H, 4.92, N, 2.97, F, 8.06. Found : C, 84.20, H, 5.07, N, 2.80.

Electrochemical Section

General Considerations. All electrochemical measurements were carried out using an EG&G PAR (Princeton Applied Research) model potentiostat/galvanostat. A three electrodes system was used. Planar working platinum and glassy carbon disks Metrohm 628-10 (diameter: 3 mm) were used as working electrodes. Their surface was mechanically polished on alumina (0.05 μm) before each measurement. All the potential values cited were measured with respect to the saturated calomel reference electrode. The auxiliary electrode was a platinum wire. Controlled potential coulometric measurements were performed using a large platinum sheet as working electrode (about 2 cm^2). All measurements have been carried out at room temperature.

Calculation of the number of electrons exchanged, n , during the electrochemical oxidation of naphthidines, as determined by chronoamperometry

The method is based on the use of a reference electroactive species, ferrocene ($n = 1$), and an ultramicroelectrode operating in conditions where both linear and spherical diffusion controls are expected to occur. In such conditions, the current-time relationship is given by equation 1.

$$i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} + \frac{nFADC}{r} \quad (1)$$

where n is the number of electron, F the Faraday constant, A the electrode surface area, D the diffusion coefficient and C the concentration of the electroactive species, while r is the electrode radius.

At short experiment times, one can consider equation (2) indicating a linear relationship between the observed current versus $1/t^{1/2}$, while at longer times the current become independent on t (Eq. 3).

$$i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \quad (2)$$

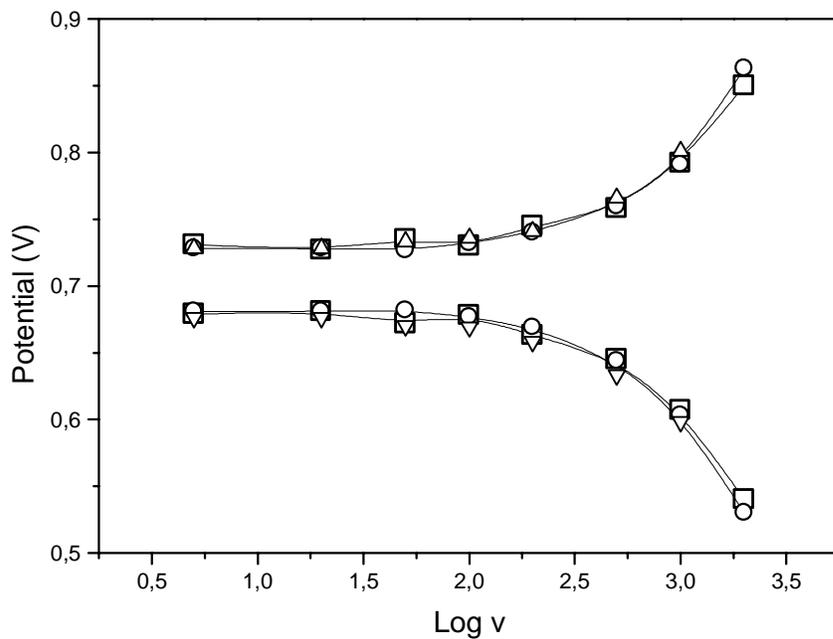
$$i = \frac{nFADC}{r} \quad (3)$$

For ferrocene, i is i_{Fc} , D is D_{Fc} and $n_{Fc} = 1$; for naphthidine, i is i_{Naph} , D is D_{Naph} and $n_{Naph} = ?$

Therefore, when using Fc and $Naph$ at the same concentration, and measuring i_{Fc} and i_{Naph} (time-independent stationary currents sampled at long times), as well as the slope of i_{Fc} vs. $1/t^{1/2}$ and i_{Naph} vs. $1/t^{1/2}$ curves (recorded at short times), the combination of equations 2&3 give enables the determination of n_{Naph} without the necessity to know any other parameter, according to equation 4.

$$n_{Naph} = \frac{i_{Fc} \times (\text{slope}\langle i_{Naph} \text{ vs. } t^{-1/2} \rangle)^2}{i_{Naph} \times (\text{slope}\langle i_{Fc} \text{ vs. } t^{-1/2} \rangle)^2} \quad (4)$$

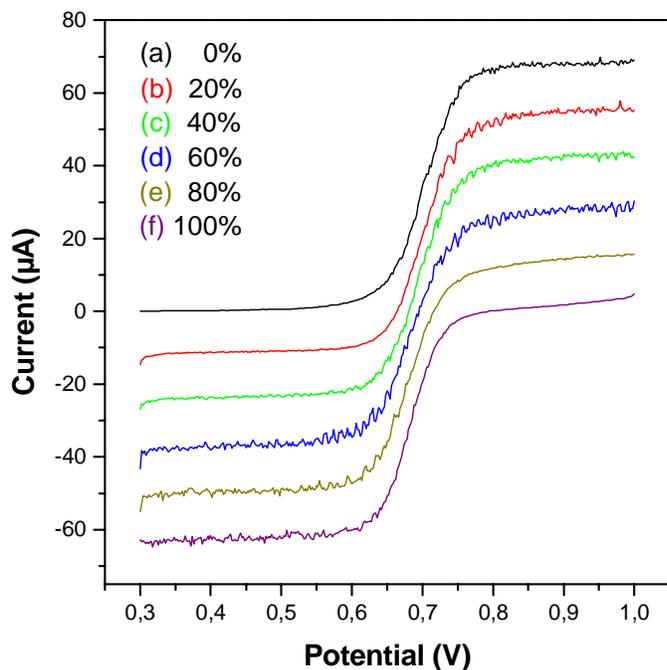
Dependence of anodic and cathodic peak potentials on scan rate (log scale) at different concentrations of naphthidine 2g



Concentrations in **2g**: 1 mM (O), 2 mM (□), and 4 mM (Δ).

The fact that no influence of concentration on peak potentials was observed supports the EE mechanism discussed in the paper and enables one to discard the possible intervention of disproportionation ($2 \mathbf{2}^{+} \rightarrow \mathbf{2} + \mathbf{2}^{2,2+}$); which is not likely to be distinguished from the pure EE mechanism by CV.⁸

Voltammetric *in situ* monitoring of the electrolysis of derivative **2g**



Linear scan voltammograms recorded during the electrolysis of compound **2g** (1×10^{-3} M in acetonitrile containing 0.1 M Bu_4NPF_6), at various completion levels: 0 % (a), 20 % (b), 40 % (c), 60 % (d), 80 % (e), and 100 % (f); potential scan rate: 50 mV s^{-1} .

In agreement with CV data, the $E_{1/2}$ value was found to be 0.71 V. As the extent of the electrochemical reaction evolved, a progressive decrease in the anodic wave was observed concomitantly to an increase of the conjugated cathodic wave. The former evolution is clearly due to the consumption of **2g** while the later is due to the generation of $\mathbf{2}^{2,2+}$ species, which was otherwise evidenced by the apparition of a deep blue color in the electrolysis cell once applying the anodic potential. This transient behavior can be also monitored by UV spectrometry. By comparing the relative intensity of anodic and cathodic waves, it appears that the diffusion coefficient of the oxidized species $\mathbf{2}^{2,2+}$ is slightly lower than that of the starting derivative **2g** (by 7%), as often observed for cations with

respect to neutral molecule (see, e.g., ferricinium with respect to ferrocene⁹). Again, $\mathbf{2}^{2.2+}$ was proven to have great stability as no significant change in the voltammetric curves recorded after electrolysis completion was observed within one day.

UV-visible spectra

UV-visible spectra of the stepwise chemical oxidation of compounds 2c-f and 2h

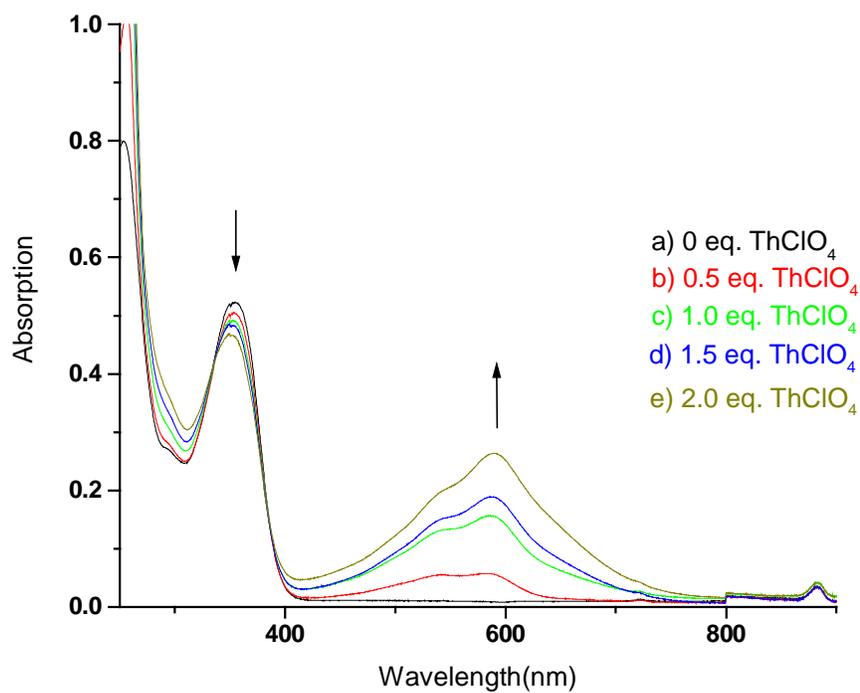


Figure 1. UV-vis spectra of the stepwise oxidation of 2c with ThClO₄ in CHCl₃ at 25°C.

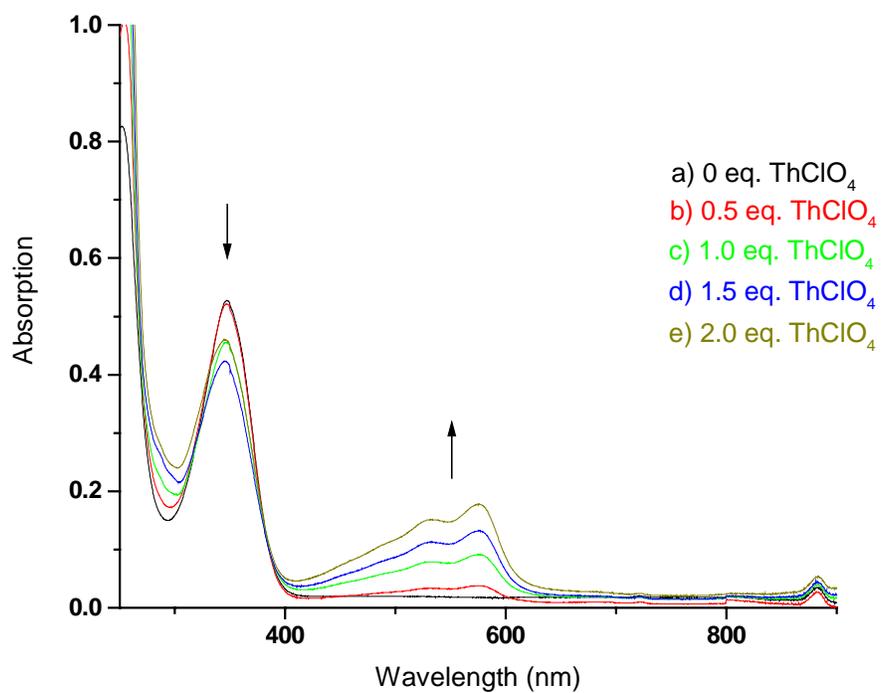


Figure 2. UV-vis spectra of the stepwise oxidation of **2d** with ThClO_4 in CHCl_3 at 25°C .

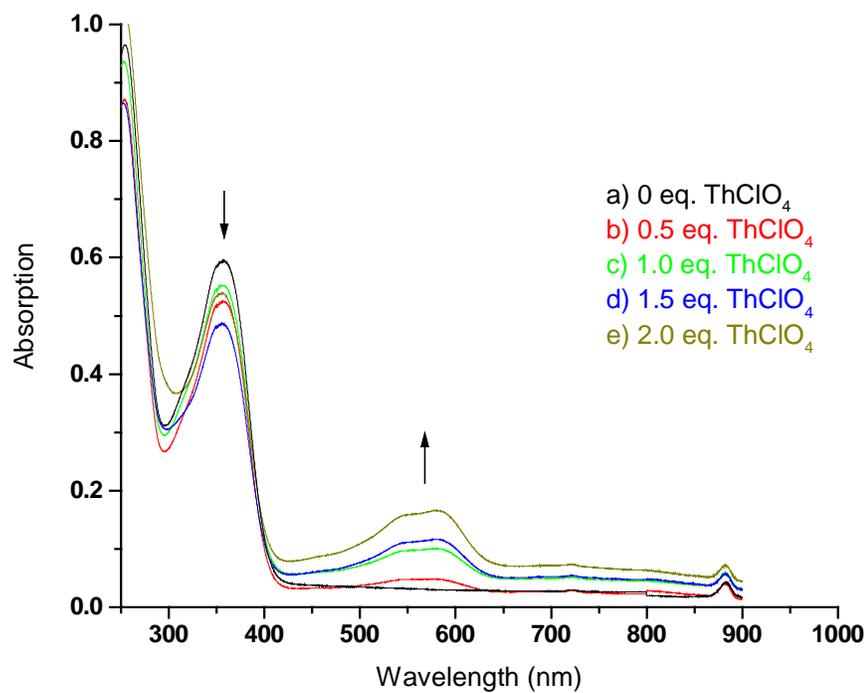


Figure 3. UV-vis spectra of the stepwise oxidation of **2e** with ThClO₄ in CHCl₃ at 25°C.

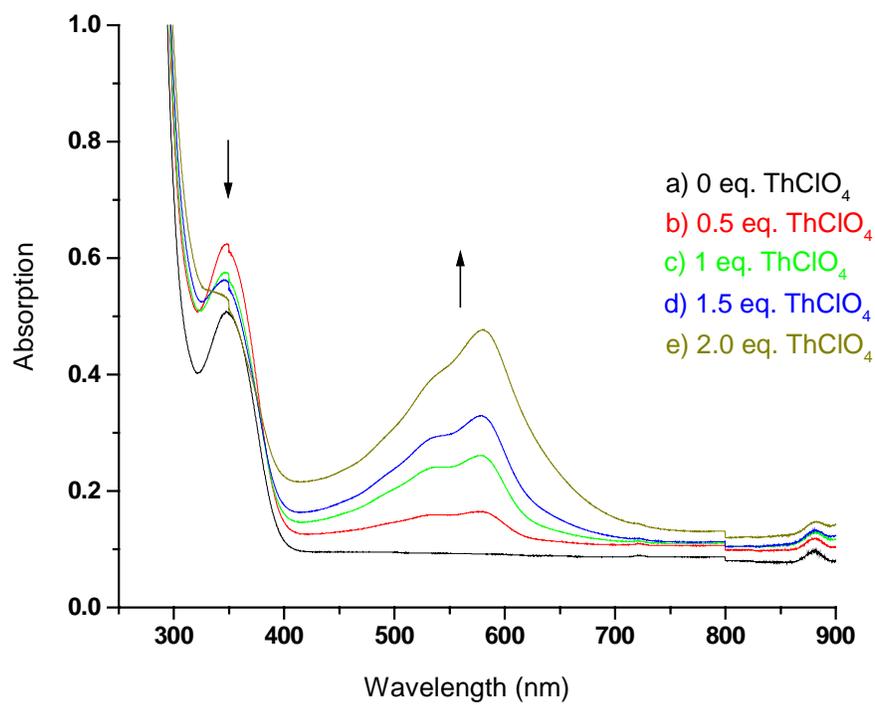


Figure 4. UV-vis spectra of the stepwise oxidation of **2f** with ThClO_4 in CHCl_3 at 25°C .

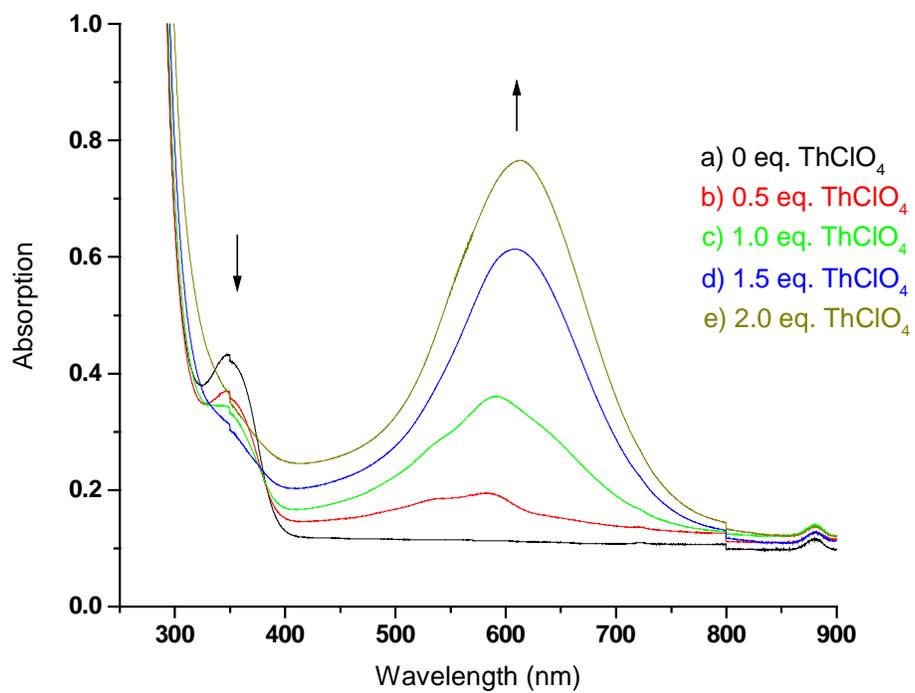
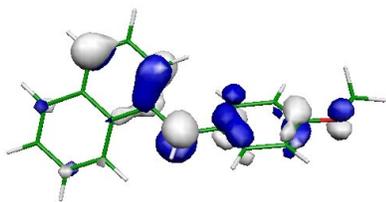


Figure 5. UV-vis spectra of the stepwise oxidation of **2h** with ThClO_4 in CHCl_3 at 25°C .

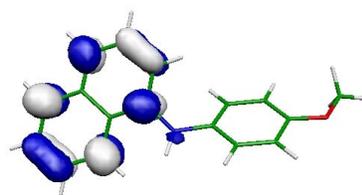
Theoretical Section

Computational details. Theoretical investigations of the ground electronic states were carried out at the DFT level using the B.04 revision of the Gaussian 03 package.¹⁰ The DFT calculations were performed using for exchange the Becke's three-parameter functional and, for correlation, the Lee, Yang and Parr functional. DFT calculations include electron correlation effects at a relatively low computational cost and the B3LYP exchange-correlation functional, which includes 20% of Hartree-Fock exchange, is known to provide accurate equilibrium geometries.¹¹ The 6-31G* basis set was used.¹² In order to match a sufficient accuracy, a tight convergence threshold was adopted for the residual forces on the atoms (1.5×10^{-5} hartree/bohr or hartree/rad). The radical cation as well as the singlet and triplet states of the diradical dication were treated as open-shell systems and their structures determined using the corresponding spin-unrestricted DFT approach. In order to include solvent effects the Integral Equation Formalism (IEF) of the Polarizable Continuum Model (PCM) was adopted.¹³

For the electronic excited states, the ZINDO approach implemented in the MOSF package¹⁴ was employed. This approach combines the Configuration Interaction schemes including Singles excitations (CIS) with the INDO/S semi-empirical Hamiltonian.¹⁵ For the two-center electron repulsion integrals, the Mataga-Nishimoto-Weiss expression is employed. The CIS method based on semi-empirical Hamiltonians has been shown to yield accurate predictions of transition energies because on the one hand, most of the low-lying excitations are dominated by single excitations and on the other hand, the parameters defining such Hamiltonians are fitted to spectroscopic data.¹⁶ The CIS approach explicitly accounts for intra- and inter-molecular charge-transfer excitations. (occupied \times unoccupied) CIS manifolds of (10 \times 10) and (20 \times 20) states were employed for **1g** and **2g**, respectively

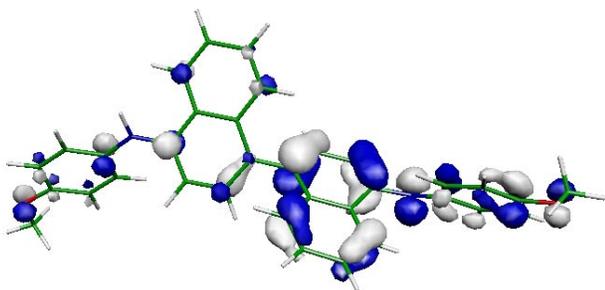


a)

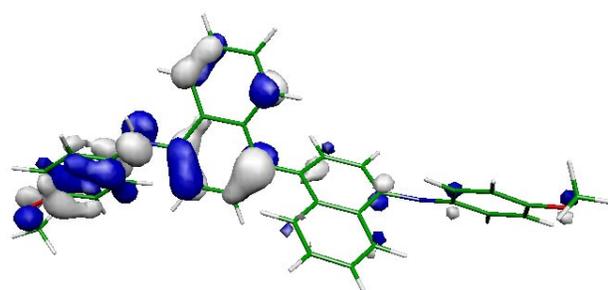


b)

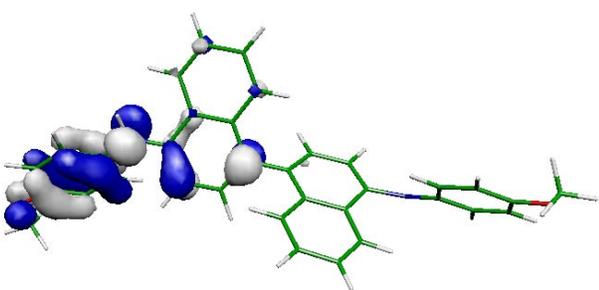
B3LYP/6-31G* Kohn-Sham orbitals (isocontour of 0.04 a.u.) for HOMO (a) and LUMO (b) of **1g**.



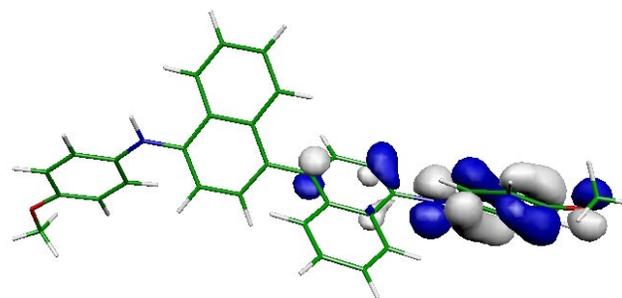
a)



b)



c)



d)

B3LYP/6-31G* Kohn-Sham orbitals (isocontour of 0.04 a.u.) for the singlet **2g^{2,2+}**. a) HOMO (α), b) HOMO (β), c) LUMO (α), d) LUMO (β).

Additional informations on the naphthidine properties as determined theoretically

Ionization energies. It is important to note that without accounting for solvation effects the difference between the two oxidation energies is much larger and amounts to 2.54 eV, while the first and second oxidation energies are 5.65 eV and 8.19 eV, respectively.

EPR spectra. In solutions, the hyperfine coupling constants (hfcc) are directly related to the spin densities at the position of the nuclei presenting a non-zero spin angular momentum. Their evaluation at the B3LYP/6-31G* level is more indicative than quantitative. For $2\mathbf{g}^+$, $\text{hfcc}(^{14}\text{N}) = 3.3 \text{ G}$ whereas $\text{hfcc}(^1\text{H}(\alpha))$, i.e. the H atoms attached to the N atoms) = -4.5G. These values are in agreement with those reported for the benzidine radical cation [$\text{hfcc}(^{14}\text{N}) = 3.60 \text{ G}$ and $\text{hfcc}(^1\text{H}(\alpha)) = -3.97 \text{ G}$] as well as for the *N,N,N',N'*-tetramethylbenzidine radical cation [$\text{hfcc}(^{14}\text{N}) = 4.8 \text{ G}$].¹⁷ In the case of the singlet and triplet di(radical cation)s $2^{2,2+}$, the amplitudes of the hfcc's do not change significantly. They amount to $\pm 2.8 \text{ G}$ for ^{14}N and $\mp 4.2 \text{ G}$ for ^1H in the singlet while to $+3.1 \text{ G}$ for ^{14}N and -4.5 G for ^1H in the triplet. In addition, many H present non negligible hfcc's value which range 0 and 1.7 G (2.3 G) for the radical cation (diradical dication), showing the delocalization of the unpaired electrons over the whole system.

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