Towards Molecular Spintronics

SP2: Heterocycles with Directly-bonded Ferrocenyl Termini as Multi-redox Systems

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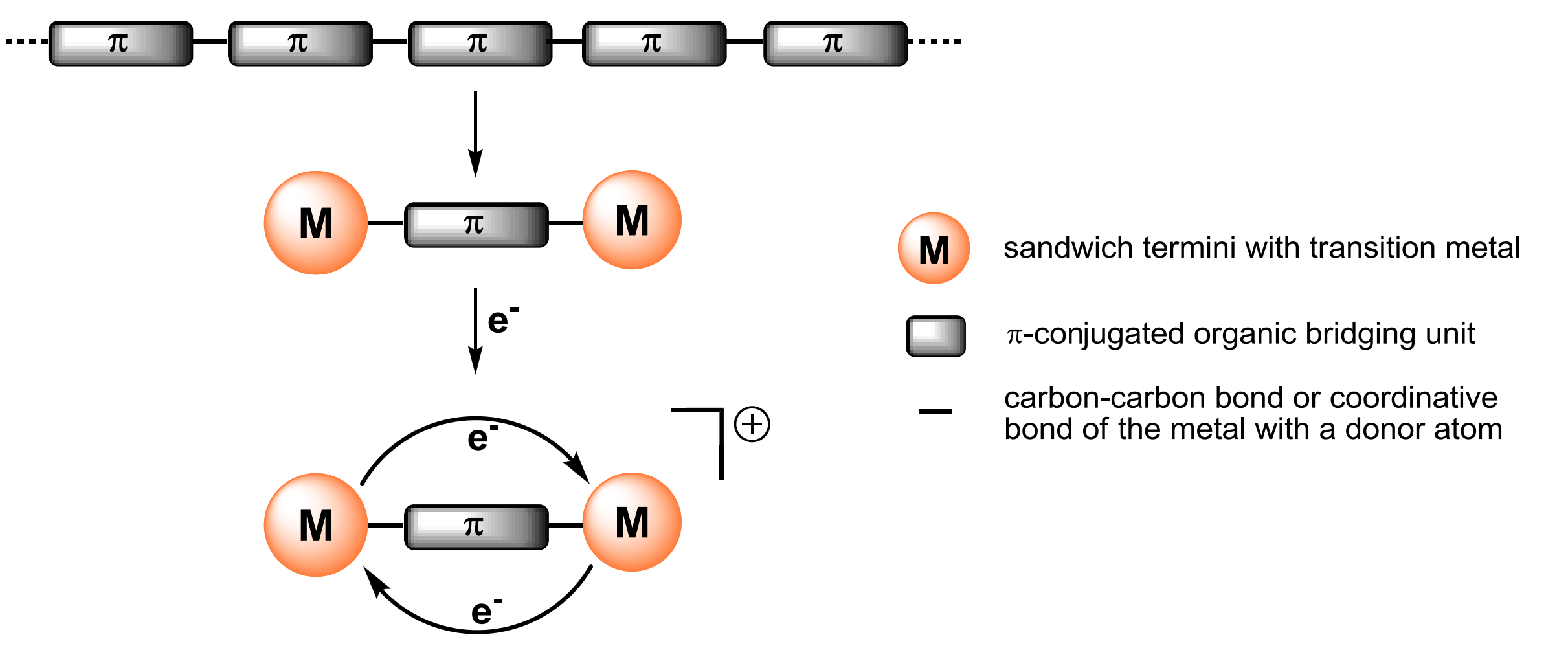
Introduction

During recent years the development of compounds with redox-active metal centres has attracted considerable attention since they can be applied as new materials with novel chemical, physical and/or electronic properties in the field of material science.[1] Therefore, homo- and heterodinuclear complexes connected by *π*-conjugated organic units were designed as simple models for molecular wires[2] and novel electro-active materials.[3] Complexes with ferrocenyls as redox-active termini are extensively explored, focusing on the electrochemical behavior and on electron transfer processes.

Motivation

To investigate electron transfer processes in molecular wires, it is usefull to study small molecules with one bridging unit between the ferrocenyl termini. Recently, we reported about the synthesis and characterization of a series of 2,5-di- and 2,3,4,5-tetraferrocenyl substituted furans, thiophenes and pyrroles.[4] In continuation of our work on ferrocenyl-functionalized heteroaromatics, we here present the design and (spectro-)electrochemical behavior of ferrocenyl-substituted oligopyrroles.

However, studies dealing with six-membered heterocyclic compounds as connector between metallocenyl units are still rare, beside few examples of Iyoda[5] and Winter[6]. In addition we present the investigation of the (spectro-) electrochemical behavior of ferrocenyl-substituted pyridines and triazine. In cooperation with SP3 the ground-state energy and the charge distribution of these systems were determined by DFT calculations.

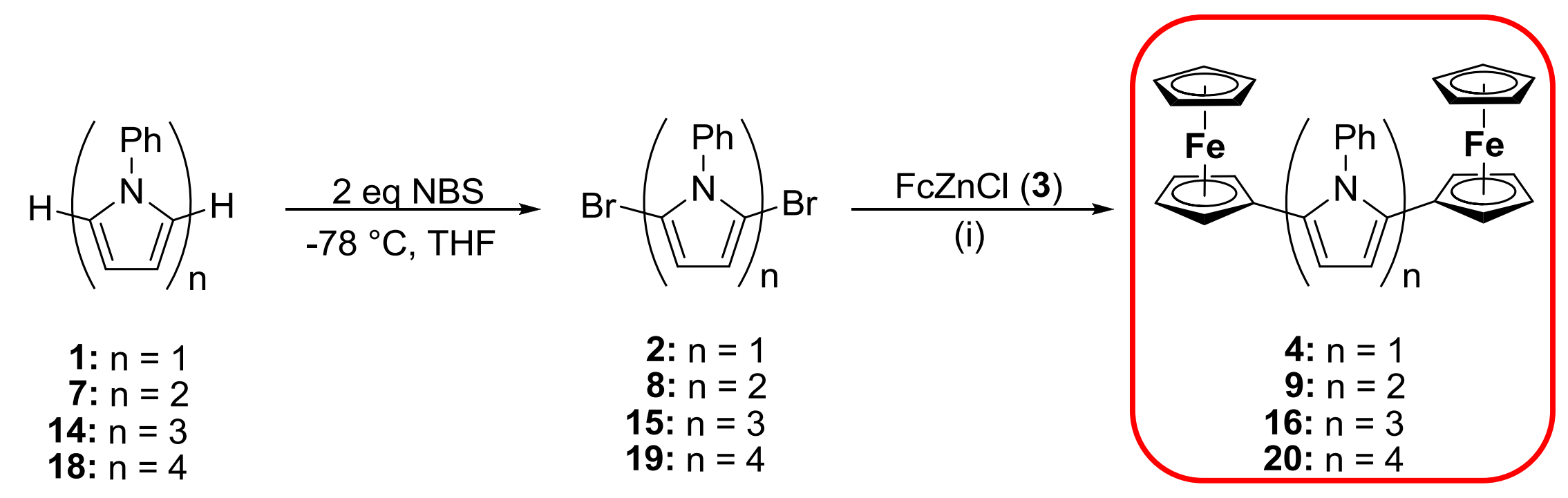


M sandwich termini with transition metal

π-conjugated organic bridging unit

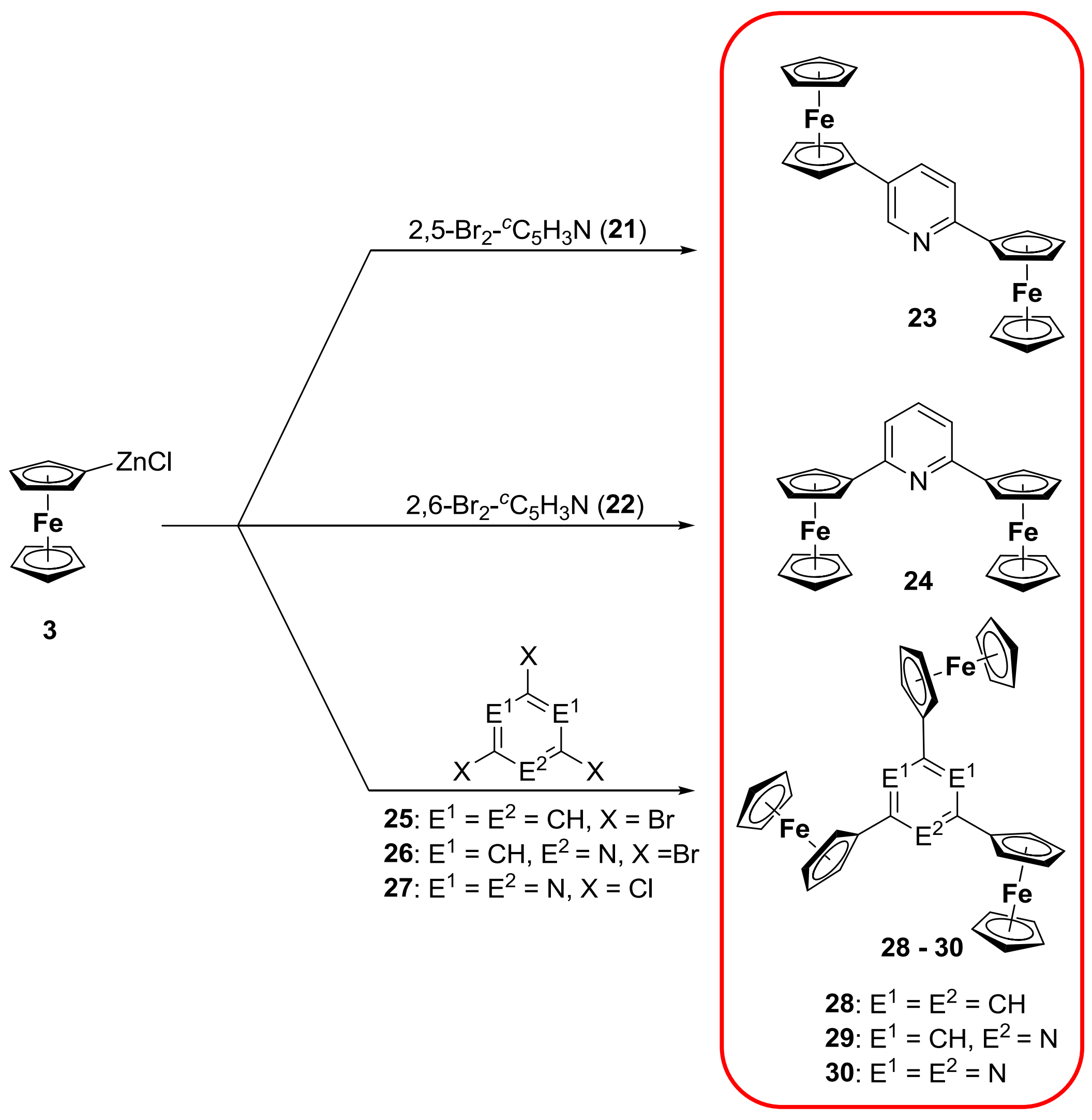
– carbon-carbon bond or coordinative bond of the metal with a donor atom

Synthesis



(**20**)

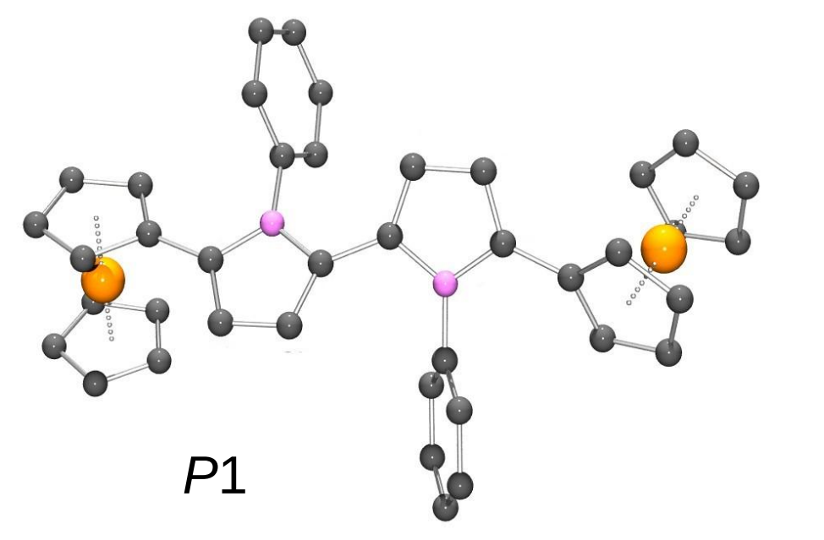
Fig. 1 *Synthesis procedure for diferrocenyl-substituted (oligo)pyrroles by Negishi C,C cross coupling reactions; (i): 60 °C, 12 h, tetrahydrofuran, 0.25 mol% [P(^{t}C$_4$H$_9$)$_2$C(CH$_3$)$_2$CH$_2$PdCl]$_2$.*



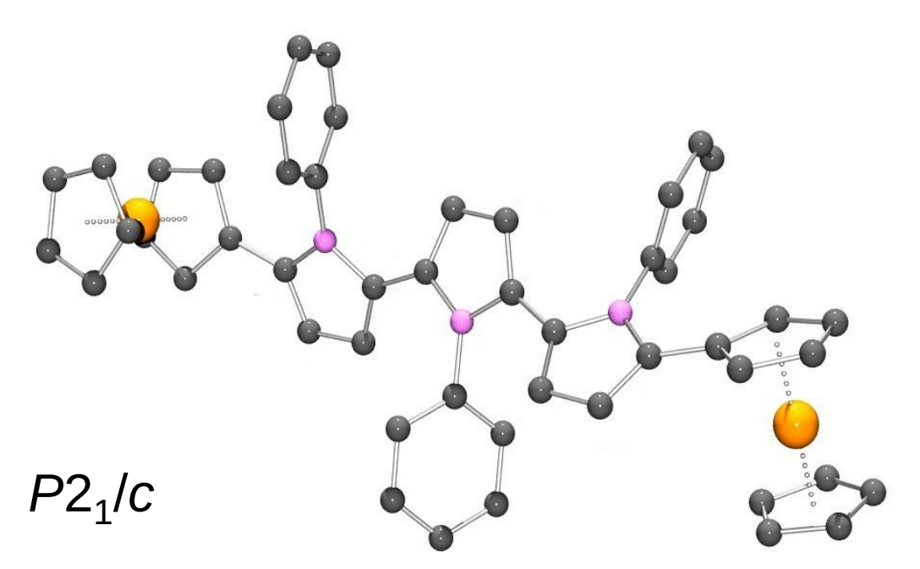
After appropriate work-up, the ferrocenyl-substituted compounds could be obtained as orange or red solids. They have been identified by NMR (^{1}H, ^{13}C{^{1}H}) and IR spectroscopy as well as elemental analysis. Additionally, high resolution ESI-TOF mass spectrometric and single crystal X-ray diffraction studies have been determined.

(**30**)

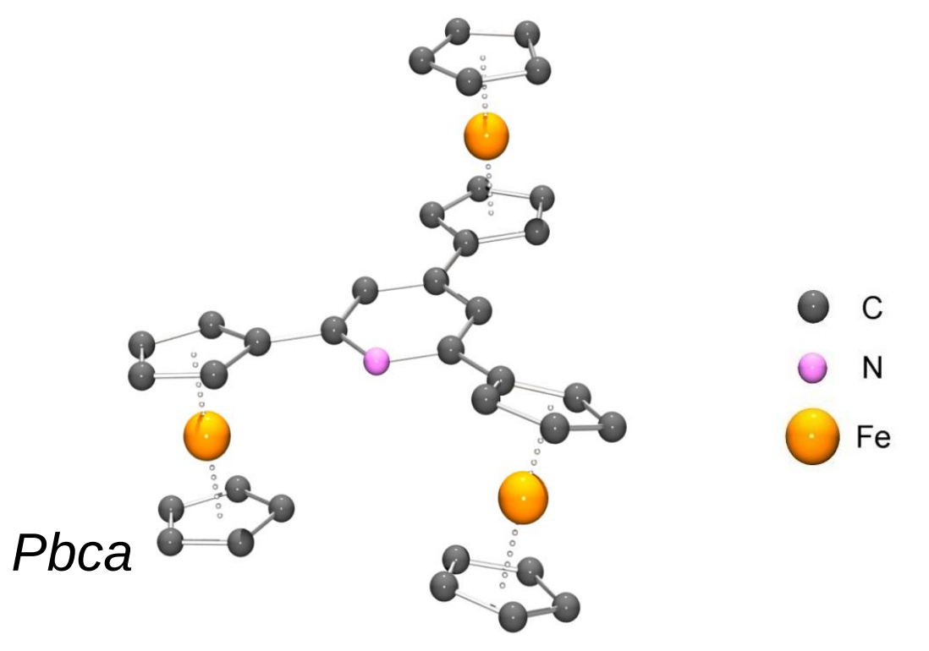
Fig. 2 *Synthesis procedure for ferrocenyl-substituted (hetero) aromatics by Negishi C,C cross coupling reactions; conditions: 60 °C, 12 h, tetrahydrofuran, 0.25 mol% [P(^{t}C$_4$H$_9$)$_2$C(CH$_3$)$_2$ CH$_2$PdCl]$_2$.*



5,5´-Diferrocenyl-*N,N*´-bisphenyl-2,2´-bipyrrole(**9**)



5,5´-Diferrocenyl-*N,N´,N´´*-trisphenyl-2,2´:5´,2´´-terpyrrole (**16**)



2,4,6-Triferrocenyl-pyridine (**29**)

Conclusion

A series of diferrocenyl oligopyrroles and di- and triferrocenyl (hetero-)aromatics have been prepared using a Negishi ferrocenylation reaction of halogenated aromatics or heteroaromatics with ferrocenyl zinc chloride.

The cyclic and square wave voltammograms highlight the electrochemical behavior of the organometallic compounds and indicate intermetallic communication. The results were proved by UV-Vis/NIR measurements. They revealed that the interactions are limited to electrostatic repulsion of the equally charged ferrocenyl termini in the di- and tri-cationic oxidation states of compounds **28 - 30** and therefore are classified as class I systems according to Robin and Day[9], while class II systems showed weak (**23** and **24**) or moderate (**4**, **9** and **16**) broad IVCT bands.

Spectro(electrochemical) Characterization

Compd.	$E^\circ_1{}'$ (mV)[a] (ΔE_p (mV))[b]	$E^\circ_2{}'$ (mV)[a] (ΔE_p (mV))[b]	$E^\circ_3{}'$ (mV)[a] (ΔE_p (mV))[b]	$E^\circ_4{}'$ (mV)[a] (ΔE_p (mV))[b]	$\Delta E^\circ_1{}'$ (mV)[c]	$\Delta E^\circ_2{}'$ (mV)[c]	$\Delta E^\circ_3{}'$ (mV)[c]
4	-245 (66)	205 (82)	-	-	450	-	-
9	-280 (72)	5 (91)	790 (97)	-	285	785	-
16	-230 (64)	-70 (68)	470 (72)	1075 (79)	160	540	605
20	-130 (66)	310 (54)	770 (60)	-	440	460	-
23	10 (80)	180 (82)	-	-	170	-	-
24	10 (64)	160 (96)	-	-	150	-	-
28	0 (62)	145 (59)	280 (87)	-	145	135	-
29	-50 (74)	120 (69)	285 (65)	-	170	165	-
30	70 (69)	210 (67)	385 (70)	-	140	175	-

[a] $E^{\circ\prime}$ = oxidation process. [b] ΔE_p = difference between oxidation and reduction potential. [c] $\Delta E^{\circ\prime}$ = potential difference between two redox processes.

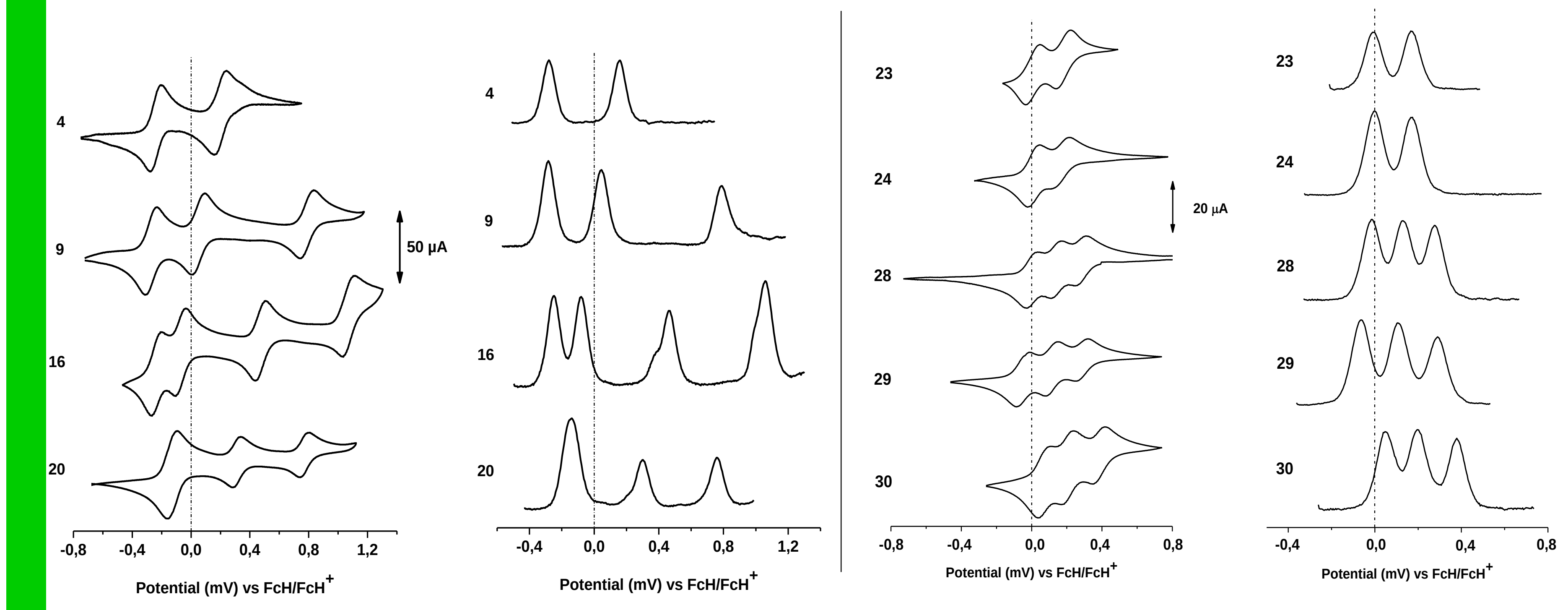
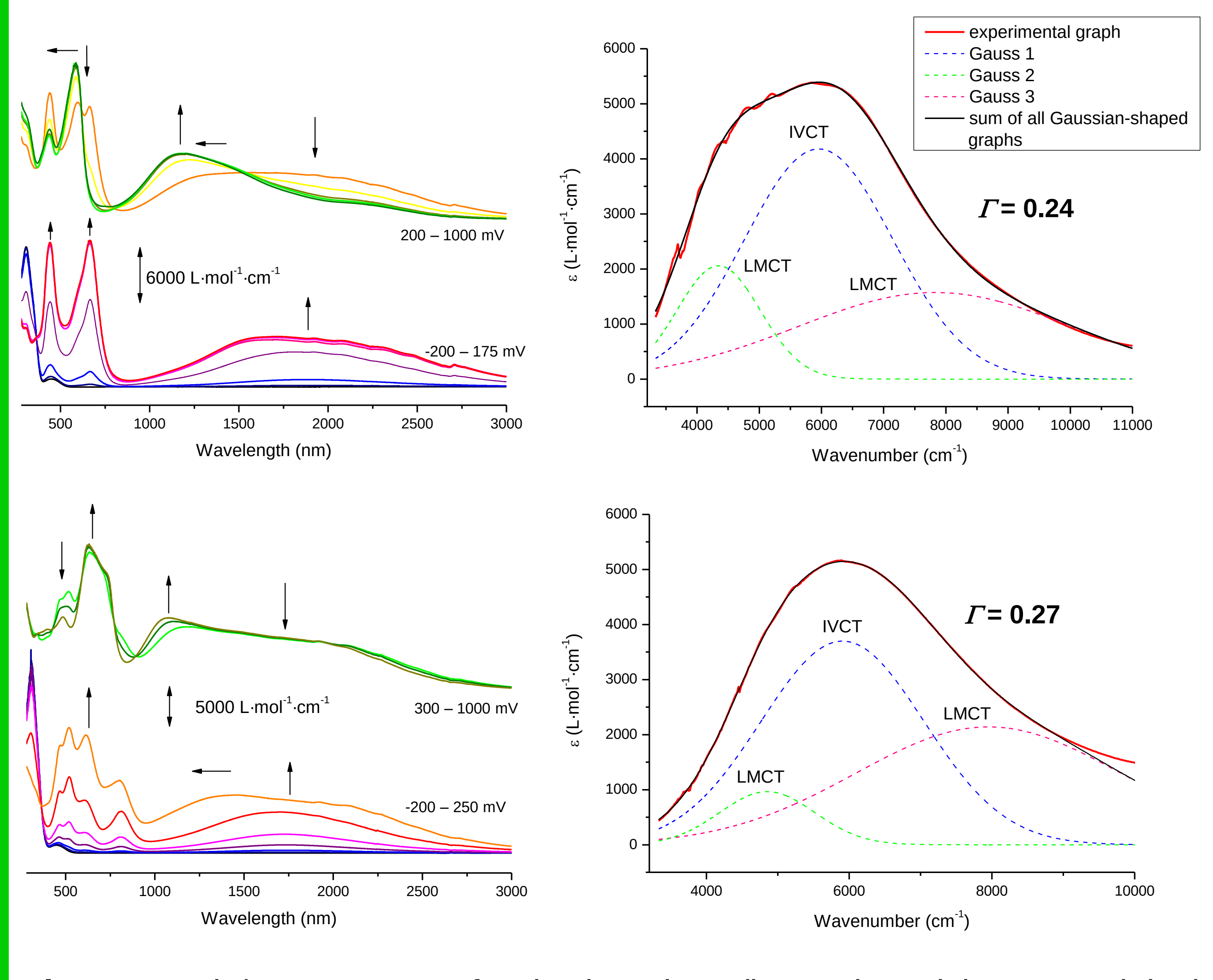


Fig. 4 *Cyclic voltammograms (scan rate: 100 mV·s^{-1}) and square-wave voltammograms (scan rate: 100 mV·s^{-1}) of dichloromethane solutions containing 1.0 mmol·L^{-1} of the substance at 25 °C. Supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol·L^{-1}).*



$$\Delta\nu_{1/2(\mathrm{theo})} = (2310\,\nu_{max})^{0.5}$$

$$\Gamma = 1 - \frac{\Delta\nu_{1/2(\mathrm{prakt})}}{\Delta\nu_{1/2(\mathrm{theo})}}$$

Band shape analyses were performed according to the Hush model for symmetric mixed valence species[7] and the classification criterion of Brunschwig, Creutz and Sutin.[8]

Fig. 6 *UV-Vis/NIR spectra of **9** (top) and **16** (bottom) at rising potentials (-200 to 1000 mV vs Ag/AgCl) (left); deconvolution of the NIR spectrum of in situ generated **9**$^+$ (175 mV, top) and **16**$^+$ (250 mV, bottom) using three Gaussian-shaped bands (right). Measurement conditions: 25 °C, dichloromethane, 0.1 mol·L^{-1} [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].*

References and Acknowledgment

[1] (a) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev*. **2002**, *31*, 168–184; (b) Low, P. J. *Dalton Trans*. **2005**, *17*, 2821–2824; (c) Ceccon, A.; Santi, S.; Orian, L.; Bisello A. *Coord. Chem. Rev.* **2004**, *248*, 683–724. [2] (a) Sato, M.; Fukui, K. *Synth. Met*, **2007**, *157*, 619–626; (b) Sato, M.; Kamine, H. *Chem. Lett.* **2009**, *38*, 924–925. [3] (a) Caballero, A.; Lloveras, V.; Curiel, D.; Tárraga, A.; Espinosa, A.; García, R.; Vidal-Gancedo, J.; Rovira, C.; Wurst, K.; Molina, P.; Veciana, J. *Inorg. Chem.*, **2007**, *46*, 825–838; (b) Robertson, N.; McGowan, G. A. *Chem. Soc. Rev.* **2003**, *32*, 96–103. [4] Hildebrandt, A.; Schaarschmidt, D.; Claus, R.; Lang, H. *Inorg. Chem.* **2011**, *50*, 10623–10632. [5] Iyoda, M.; Kondo, T.; Okabe, T.; Matsuyama, H.; Sasaki, S.; Kuwatani, Y. *Chem. Lett.* **1997**, 35–36. [6] Kowalski, K.; Winter, R. F. *J. Organomet. Chem.* **2009**, *694*, 1041–1048. [7] Hush, N. S. *Electrochim. Acta*, **1968**, *13*, 1005-1023. [8] Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev*. **2002**, *31*, 168-184. [9] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.*, **1967**, *10*, 247–422.

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