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Ferrocene-quinoxaline Y-shaped chromophores as fascinating second-order NLO building blocks for long lasting highly active SHG polymeric films

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The first example of a Y-shaped ferrocene quinoxaline derivative with a surprisingly high and stable second harmonic generation (SHG) response in composite polymeric films is reported. The interesting quadratic hyperpolarizability values of different substituted Y-shaped chromophores are also investigated in solution by the EFISH technique.

Materials with second-order nonlinear optical (NLO) properties are of great interest since they can be used for various important applications such as optical communication, optical data processing and storage and electro-optical devices.¹

Organic chromophores with particular shapes (H,² V,³ Y,⁴ X⁵, T⁶ and star⁷ type) are interesting for electro-optic applications and their arrangement assures efficient intramolecular charge transfer (ICT) between the donor and acceptor moieties and generates push-pull system featuring low-energy and intense CT absorption.⁸ Due to the ICT, push-pull Donor- π -Acceptor (D- π -A) molecules possess distinct nonlinear optical (NLO) properties.

Metal complexes, compared to organic compounds, can offer additional flexibility thanks to the presence of NLO-active charge-transfer transitions between the metal and the ligands usually of high intensity and at relatively low energy, tunable by nature, oxidation state and coordination sphere of the metal center.⁹

Heteroaromatic moieties incorporated into an NLO chromophore may act as auxiliary D or A and further improve the optical nonlinearity of the chromophore. Quinoxalines/pyrazines have been widely used in chromophore systems as strong electron-acceptor because of their high electron deficiency originated from the two symmetric unsaturated nitrogen atoms that lower the π^* level of the conjugated system.¹⁰ Limited information on the Y-shaped chromophores based on a quinoxaline moiety for NLO and dye-sensitized solar cell (DSSC) is available in literature.¹¹ In particular Bures *et al.*, studied structure-property relationships and NLO properties for different substituted pyrazine push-pull

chromophores with various π -linkers.^{5b,6,11b}

In the field of NLO, ferrocene derivatives have been deeply investigated and have played the role of electron-donor in charge transfer processes in chromophores where ferrocene was linked to an acceptor moiety.^{9b,12}

Although ferrocene-quinoxaline based Y-shaped chromophores, recently reported by Kumar *et al.*, show interesting DSSC performance,¹³ and their NLO properties have never been investigated. This type of organometallic based Y-shaped chromophores structure allows a good coupling between the *d* orbitals of the metal and π^* system of the quinoxaline moiety that could afford a significant NLO response controlled by low-energy metal ligand charge transfer (MLCT) transitions.

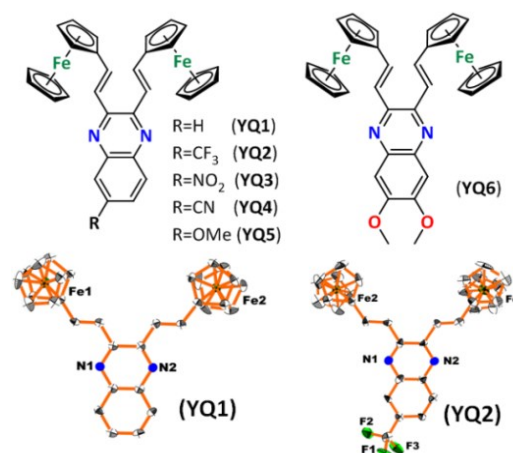


Figure 1. Chemical structures of Y-shaped ferrocene-based chromophores **YQ1–YQ6** and single crystal X-ray structures of chromophores **YQ1** and **YQ2** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Keeping this in mind, we have synthesized Y-shaped chromophores by condensation of an 1,6-Bisferrocenyl-hexa-1,5-diene-3,4-dione with a substituted 1,2-diamino compound; this is one of the most versatile method and was used for the construction of quinoxaline derivatives **YQ1**, **YQ2**, **YQ5**, **YQ6**; for **YQ3** and **YQ4** a different synthetic strategy was used as shown in scheme S1.

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The Y-shaped substituted quinoxaline derivatives **YQ1-YQ6** were characterized by using FT-IR, ¹H-NMR, mass and single crystal X-ray diffraction techniques (ESI[†]). The single crystal X-ray structure of **YQ1** and **YQ2** (Fig. 1) shows a Y-shaped structure and the ferrocene moieties are facing antennae type. The structural parameters obtained from X-ray analysis closely matches with optimized structures obtained from density functional theory (DFT) studies at B3LYP/6-31+G** level of theory (ESI[†]) except that there is a slight difference in the values of the dihedral angles with respect to substituents (H and CF₃). This may be due to the solid state packing and the associated intermolecular hydrogen bonding (ESI[†]).

The absorption spectra in CH₂Cl₂ of chromophores **YQ1-YQ6** show variably intense CT absorption bands as reported in Fig. 2. All molecules depict prominent absorption bands in the UV region which can safely be ascribed to a high energy ligand-centred (ICT transition) π-π* electronic transition. The other bands in the visible region can be assigned to other localized excitations with a lower energy produced either by two nearly degenerate transitions, a Fe(II) *d-d* transition (assigned to ¹E_{1g} ← ¹A_{1g}) or by a MLCT process (*dπ-π**).¹⁴ By increasing the strength of R as an electron withdrawing group on the quinoxaline scaffold, a bathochromic shift is observed. The detailed absorption bands and their energy gap are given in Table 1.

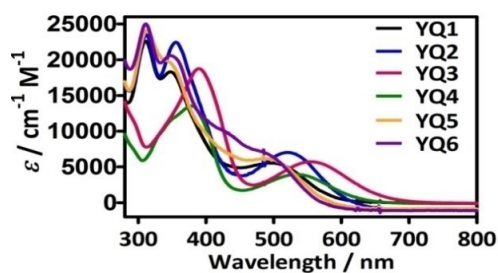


Figure 2. Absorption spectra of **YQ1-YQ6** in CH₂Cl₂ at 298 K.

To gain insight into the structural and electronic properties of chromophores **YQ1-YQ6**, we performed DFT and time-dependent DFT (TD-DFT) calculations using Gaussian 09 software.¹⁵ Main optimized geometrical parameters and calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, absorption maxima (λ_{\max}), are reported in Table 1 (ESI[†]). The lowest energy electronic transitions for all the quinoxaline chromophores are originated from the HOMO to LUMO. The HOMO-LUMO energy gap decreases by increasing the strength of acceptor, and the experimental results confirm this trend as evidenced by a red shift of the MLCT band. The density plots of HOMO and LUMO levels and their energy gaps are influenced by electron donor ferrocene, π-spacer and acceptor quinoxaline derivative strength. The HOMO is mainly localized on the ferrocene moiety and π-spacer double bond, whereas the electron density in the LUMO is mainly localized on the substituted quinoxaline moiety (Fig. 3). The HOMO energies of chromophores **YQ1-YQ6** are quite similar (-5.6 to -5.3 eV) while their LUMO energies are influenced by virtue of the nature of R substituents. The biggest destabilizations are observed when R is an electron-donor substituent (**YQ5** and **YQ6**) reaching -2.80 to 2.24 eV. Therefore, the increased HOMO - LUMO gap calculated for all the chromophores is essentially related to LUMO destabilization. The calculated absorption maxima of chromophores are originated by

single HOMO - LUMO transitions (at 3.12 to 2.64 eV / 397 to 469 nm) based on the DFT calculations. The theoretically observed trend is comparable with experimental values. The absolute values vary by the range of 100nm with experimental values which is due to the limitation in the basis set used for calculations. The calculated data and main transitions involved in the principle orbitals are given as density plot in ESI[†].

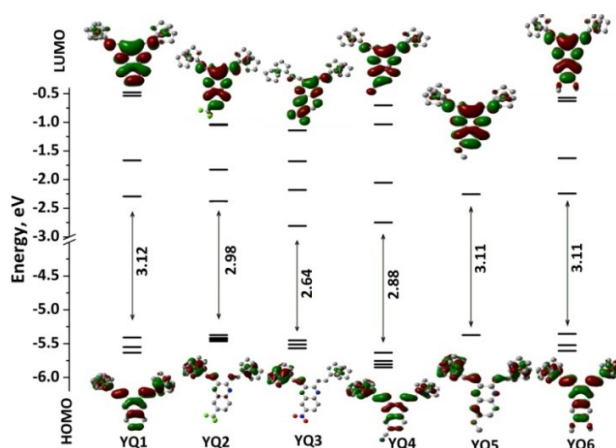


Figure 3. Schematic representation of the energy levels of chromophores **YQ1-YQ6** at B3LYP/6-31+G** level of theory. Iso-density surface plots (isodensity contour: 0.02) of HOMO and LUMO molecular orbitals are also shown.

Here we report the second-order NLO properties in CHCl₃ solution of all the chromophores, using the electric field induced second harmonic (EFISH) generation technique.¹⁶ This technique offers a valuable alternative to Hyper-Rayleigh scattering (HRS) which suffers from the limitation of possible overestimation of values of the quadratic hyperpolarizability due to multiphoton fluorescence. EFISH can provide direct information on the intrinsic molecular NLO properties through eqn. (1):

$$\gamma_{\text{EFISH}} = (\mu\beta_{\text{EFISH}}/5kT) + \gamma(-2\omega, \omega, \omega, 0) \quad (1)$$

where $\mu\beta_{\text{EFISH}}/5kT$ is the dipolar orientational contribution to the molecular nonlinearity, and $\gamma(-2\omega, \omega, \omega, 0)$, the third order polarizability at frequency ω of the incident light, is a purely electronic cubic contribution to γ_{EFISH} which can usually be neglected when studying the second-order NLO properties of dipolar compounds. Chromophores **YQ1-YQ6** are characterized by good to excellent values of $\mu\beta_{\text{EFISH}}$ (-430 to -960 × 10⁻⁴⁸esu), see Table 1, working in CHCl₃ at a concentration of 10⁻³ M with a non-resonant incident wavelength of 1.907 μm, obtained by Raman-shifting under high H₂ pressure by using a Q-switched, mode-locked Nd³⁺:YAG laser. The largest $\mu\beta_{\text{EFISH}}$ values are observed for CF₃ (**YQ2**) and NO₂ (**YQ3**) derivatives. In order to obtain the projection along the dipole moment axis of vectorial component of tensor of the quadratic hyperpolarizability (β_{EFISH}), it is necessary to know the dipole moment, μ . So in this work, we have calculated the theoretical dipole moments (B3LYP/6-31+G**) of all the chromophores. For comparison, we have also experimentally determined the dipole moments in CHCl₃ for compounds **YQ2**, **YQ3**, and **YQ4** (Table 1) using the Guggenheim's method.¹⁷ Experimental values follow the same trend of theoretical ones but are lower than the calculated dipole moments, in accordance with the literature.¹⁸

Table 1. Photophysical data and second order NLO properties of the investigated chromophores **YQ1-YQ6**.

Sample	$\lambda_{\max}^{\text{HE}}$ [nm (eV)] / ϵ ($\times 10^3$) [$\text{M}^{-1} \text{cm}^{-1}$] ^a	$\lambda_{\max}^{\text{LE}}$ [nm (eV)] / ϵ ($\times 10^3$) [$\text{M}^{-1} \text{cm}^{-1}$] ^a	HOMO ^b (eV)	LUMO ^b (eV)	λ_{\max} , [nm (eV)] ^b	$\mu^{b,d}$ ($\times 10^{-18}$ esu)	$\mu\beta^e$ ($\times 10^{-48}$ esu)
YQ1	349 (3.55) /17.5	498 (2.48) /0.55	-5.40	-2.29	397 (3.12)	3.4	-790
YQ2	356 (3.48) /22.1	522 (2.37) /0.68	-5.37	-2.37	413 (2.99)	5.9	-960
YQ3	389 (3.18) /18.7	558 (2.22) /0.57	-5.45	-2.80	469 (2.64)	6.3	-820
YQ4	379 (3.27) /12.8	536 (2.31) /0.39	-5.63	-2.74	430 (2.88)	5.5	-560
YQ5	350 (3.54) /20.1	501 (2.47) /0.61	-5.37	-2.25	397 (3.11)	1.1	-580
YQ6	352 (3.52) /19.8	499 (2.48) /0.64 ^c	-5.35	-2.24	398 (3.11)	1.3	-430

^a experimental data (HE= High energy, LE = low energy), ^b theoretical data calculated with B3LYP/6-31+G** theory, ^c shoulder, ^d for compounds **YQ2**, **YQ3** and **YQ4**, the values were also determined experimentally in CHCl_3 (3.3 , 3.4 and 2.1×10^{-18} esu respectively). ^e In anhydrous CHCl_3 estimated uncertainty in EFISH measurements $\pm 10\%$.

The investigated chromophores show a “push-pull” Y-shaped structure which is the origin of a non-zero dipole moment and it is directed from the symmetrical ferrocenyl moiety as a positive pole to quinoxaline moiety as a negative pole (ESI[†]).

The substituents are responsible for the different ground state dipole moments: going from **YQ1** (R=H) to **YQ2-YQ4** (R=electron withdrawing group) there is an increase of the dipole moment, whereas going from **YQ1** (R=H) to **YQ5-YQ6** (R=electron donor group) a decrease of the dipole moment occurs (Table 1). These data show that the origin of high $\mu\beta$ values of **YQ2** and **YQ3** is a particularly high dipole moment. Surprisingly, although second order NLO properties both in solution and in the solid-state of many ferrocene derivatives have been investigated,^{9b} only a few works of thin films of pure ferrocene or ferrocene derivatives have been published.¹⁹ Host-guest polymethylmethacrylate (PMMA) films with ferrocene were reported²⁰ but the films were studied for their luminescent properties only. To our knowledge, no SHG measurements of PMMA films with ferrocene guests have been reported. When dipolar chromophores are introduced into polymeric systems as dopants, high polar push-pull structure usually leads to centrosymmetric alignment, due to the strong electronic interactions. However, only those materials lacking centrosymmetry could exhibit nonzero macroscopic second-order susceptibility. A convenient way to achieve the non-centrosymmetric alignment of chromophore moieties with high μ is to heat the film to a temperature near the glass transition temperature of polymer (T_g) in the presence of an electric field, leading to the poling-induced non-centrosymmetric alignment of chromophores.²¹

The high quadratic hyperpolarizability value of chromophore **YQ2** in solution prompted us to investigate its potential as a molecular building block for composite films with SHG properties. It was dispersed both in PMMA and polystyrene (PS) matrices (5% wt. of chromophore with respect to the matrix) and oriented by poling (ESI[†]). The corona wire poling dynamics of the SHG behavior of polystyrene and PMMA composite film are reported in Fig. 4. The UV-Vis absorption spectra after and before poling and the SEM images of **YQ2** in polystyrene and in PMMA films are reported in Figures S1 and S3 respectively. The second order NLO coefficient d_{33} for poled films was obtained by following the standard Maker fringe technique (see ESI[†]).

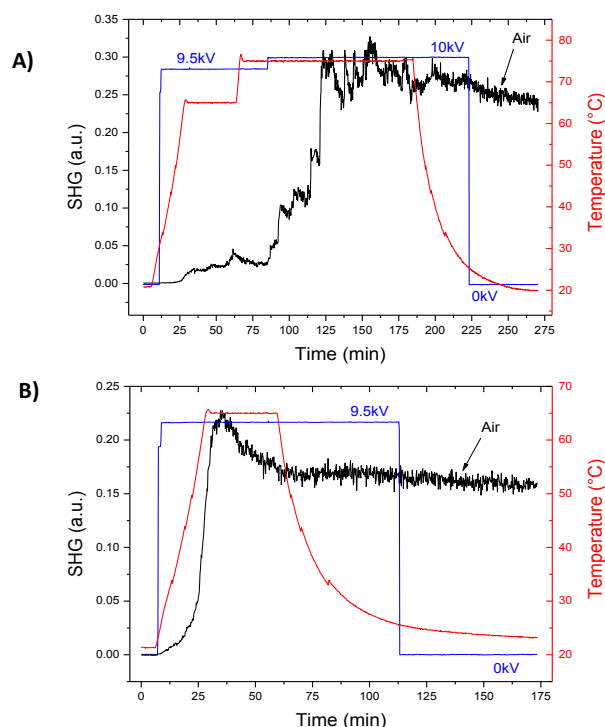


Figure 4. In situ corona-wire poling dynamics for chromophore **YQ2** in polystyrene (A) and in PMMA (B) thin films. The film thicknesses are $1.85 \mu\text{m}$ and $0.85 \mu\text{m}$ respectively.

We found excellent d_{33} values both in PS and in PMMA (a d_{33} of 2.96 pm/V and 5.27 pm/V respectively. For d_{33} calculation see ESI[†]); remarkably to our knowledge, the d_{33} value in PMMA is the highest ever reported for a host/guest system based on an organometallic chromophores. Surprisingly, the SHG signal remains unchanged also when the electric field is switched off. Its stability is remarkable, after four months we found a d_{33} value of 1.72 pm/V , with a stability of 33%. It is worth pointing out that the PMMA system gives an SHG response higher than polystyrene, but a higher stability (50%) is reached using polystyrene as a matrix (d_{33} of 1.47 pm/V).

In conclusion, the reported Y-shaped chromophores containing ferrocene and a quinoxaline core have good second order nonlinear optical properties in solution and the really high d_{33} value of the host/guest film in PMMA of **YQ2** makes those chromophores fascinating building blocks to obtain long lasting NLO-active polymeric films.

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Notes and References

- (a) J. Zyss and D. S. Chemla, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, Elsevier, 1987, pp. 23–191; (b) N. P. Prasad and D. J. Williams, In *Introduction to Nonlinear Optical Effects in molecules and Polymers*; Wiley, 1991; (c) J. Zyss, In *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press: Boston, 1994; (d) D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195–242; (e) S. R. Marder, *Chem. Commun.*, 2006, 131–134; (g) G. S. He, L.-S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245–1330; (h) J. Zyss in *Molecular Nonlinear Optics: Materials, Physics, and Devices*, Academic Press, Boston, 2013.
- W. Wu, C. Ye, J. Qin and Z. Li, *Chempluschem*, 2013, **78**, 1523–1529.
- (a) F. Momicchioli, G. Ponterini and D. Vanossi, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15576–89; (b) Andreu, E. Galán, J. Garín, V. Herrero, E. Lacarra, J. Orduna, R. Alicante and B. Villacampa, *J. Org. Chem.*, 2010, **75**, 1684–92.
- M. Pokladko-Kowar, N. Nosidlak, E. Gondek, I. V. Kityk, F. Bureš, J. Kulhánek and P. Karasiński, *Opt. Quantum Electron.*, 2016, **48**, 82.
- (a) H. Kang, G. Evmenenko, P. Dutta, K. Clays, K. Song and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 6194–205; (b) L. Dokládlová, F. Bureš, W. Kuznik, I. V. Kityk, A. Wojciechowski, T. Mikysek, N. Almonasy, M. Ramaiyan, Z. Padělková, J. Kulhánek and M. Ludwig, *Org. Biomol. Chem.*, 2014, **12**, 5517–27.
- P. Solanke, F. Bureš, O. Pytela, M. Klikar, T. Mikysek, L. Mager, A. Barsella and Z. Růžičková, *European J. Org. Chem.*, 2015, 5339–5349.
- W. Wu, C. Wang, C. Zhong, C. Ye, G. Qiu, J. Qin and Z. Li, *Polym. Chem.*, 2013, **4**, 378–386.
- (a) S. Matsumoto, M. Akazome, S. Qu, T. Kobayashi, M. Kanehiro and K. Ogura, *Heterocycles*, 2010, **80**, 645; (b) W. Chen, T. Salim, H. Fan, L. James, Y. M. Lam and Q. Zhang, *RSC Adv.*, 2014, **4**, 25291; (c) C. Y. Jung, C. J. Song, W. Yao, J. M. Park, I. H. Hyun, D. H. Seong and J. Y. Jaung, *Dye. Pigment.*, 2015, **121**, 204–210; (d) K. Pei, Y. Wu, H. Li, Z. Geng, H. Tian and W.-H. Zhu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 5296–5304.
- (a) I. D. L. Albert, T. J. Marks and M. A. Ratner, *J. Am. Chem. Soc.*, 1997, **119**, 6575–6582; (b) S. Di Bella, C. Dragonetti, M. Pizzotti, D. Roberto, F. Tessore, R. Ugo, in *Topics in Organometallic Chemistry 28. Molecular Organometallic Materials for Optics* (eds. H. Le Bozec, V. Guerschais), 1–55, Springer Verlag Berlin Heidelberg, 2010; (c) A. Valore, M. Balordi, A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, T. Benincori, G. Rampinini, F. Sannicolò, F. Demartin, *Dalton Trans.*, 2010, **39**, 10314–10318; (d) E. Rossi, A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, A. Valore, J.A.G. Williams, M.G. Lobello, F. De Angelis, S. Fantacci, I. Ledoux-Rak, A. Singh, J. Zyss, *Chem. Eur. J.*, 2013, **19**, 9875–9883.
- (a) T. Yamamoto, T. Kanbara, N. Ooba and S. Tomaru, *Chem. Lett.*, 1994, 1709–1712; (b) C. Dragonetti, M. Pizzotti, D. Roberto, S. Galli, *Inorg. Chim. Acta*, 2002, **330**, 128–135; (c) M. Pizzotti, R. Ugo, D. Roberto, S. Bruni, P. Fantucci, C. Rovizzi, Organometallics, 2002, **21**, 5830–5840; (d) Y. Wu and W. Zhu, *Chem. Soc. Rev.*, 2013, **42**, 2039–2058.
- (a) D. W. Chang, H. J. Lee, J. H. Kim, S. Y. Park, S. M. Park, L. Dai and J. B. Baek, *Org. Lett.*, 2011, **13**, 3880–3883; (b) F. Bureš, H. Čermáková, J. Kulhánek, M. Ludwig, W. Kuznik, I. V. Kityk, T. Mikysek and A. Růžička, *European J. Org. Chem.*, 2012, 529–538; (c) K. Pei, Y. Wu, A. Islam, S. Zhu, L. Han, Z. Geng and W. Zhu, *J. Phys. Chem. C*, 2014, **118**, 16552–16561;
- (a) S. Scuppa, L. Orian, D. Dini, S. Santi, M. Meneghetti, *J. Phys. Chem. A*, 2009, **113**, 9286–9294; (b) M. Zaarour, A. Singh, C. Latouche, J.A.G. Williams, I. Ledoux-Rak, J. Zyss, A. Boucekkine, H. Le Bozec, V. Guerschais, C. Dragonetti, A. Colombo, D. Roberto, A. Valore, *Inorg. Chem.*, 2013, **52**, 7987–7994.
- R. Chauhan, M. Shahid, M. Trivedi, D. P. Amalnerkar and A. Kumar, *Eur. J. Inorg. Chem.*, 2015, 3700–3707.
- (a) C. T. Sanderson, J. A. Quinlan, R. C. Conover, M. K. Johnson, M. Murphy, R. A. Dluhy and C. Kotal, *Inorg. Chem.*, 2005, **44**, 3283–3289; (b) S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715–3723.
- (a) M. J. Frisch, et al., Gaussian09 Rev. C.01, Gaussian, Inc., Wallingford CT, 2009; (b) R. L. Martin, *J. Chem. Phys.*, 2003, **118**, 4775.
- (a) B.F. Levine, C.G. Bethea *J. Chem. Phys.*, 1975, **63**, 2666–2682; (b) I. Ledoux, J. Zyss, *J. Chem. Phys.*, 1982, **73**, 203–213
- E. A. Guggenheim, *Trans. Faraday Soc.* 1949, **45**, 714–720.
- V. Calabrese, S. Quici, E. Rossi, E. Criati, C. Dragonetti D. Roberto, E. Tordin, F. De Angelis, F. Fantacci, *Chem. Comm.* 2010, **46**, 8374–8376.
- (a) A. Matei, C. Constantinescu, V. Ion, B. Mitu, I. Ionita, M. Dinescu, C. Vasiliu, A. Emandi, *J. Organomet. Chem.*, 2014, **751**, 638–643; (b) C. Constantinescu, A. Matei, V. Ion, B. Mitu, I. Ionita, M. Dinescu, C. R. Luculescu, C. Vasiliu, A. Emandi, *Applied Surface Science*, 2014, **302**, 83–86.
- (a) D. Basak, B. Mallik, *Synthetic Metals*, 2006, **156**, 176–184; (b) A. Thander, B. Mallik, *Solid State Commun.* 1999, **111**, 341–346; (c) A. Thander, B. Mallik, *Chem. Phys. Lett.* 2000, **330**, 521–527; (d) A. Thander, B. Mallik, *Solid State Commun.* 2002, **121**, 159–164; (e) D. Basak, B. Mallik, *Synthetic Metals*, 2004, **146**, 151–158.
- (a) F. Nisic, A. Colombo, C. Dragonetti, M. Fontani, D. Marinotto, S. Righetto, D. Roberto and J. A. G. Williams, *J. Mater. Chem. C*, 2015, **3**, 7421–7427; (b) D. Marinotto, S. Proutière, C. Dragonetti, A. Colombo, P. Ferruti, D. Pedron, M.C. Ubaldi, S. Pietralunga, *J. Non-Cryst. Solids*, 2011, **357**, 2075–2080; (c) D. Marinotto, R. Castagna, S. Righetto, C. Dragonetti, A. Colombo, C. Bertarelli, M. Garbugli, G. Lanzani, *J. Phys. Chem. C*, 2011, **115**, 20425–20432; (d) A. Colombo, C. Dragonetti, D. Marinotto, S. Righetto, D. Roberto, S. Tavazzi, M. Escadeillas, V. Guerschais, H. Le Bozec, A. Boucekkine, C. Latouche, *Organometallics*, 2013, **32**, 3890–3894; (e) J. Boixel, V. Guerschais, H. Le Bozec, D. Jacquemin, A. Amar, A. Boucekkine, A. Colombo, C. Dragonetti, D. Marinotto, D. Roberto, S. Righetto, R. De Angelis, *J. Am. Chem. Soc.*, 2014, **136**, 5367–5375; (f) C. Dragonetti, A. Colombo, D. Marinotto, S. Righetto, D. Roberto, A. Valore, M. Escadeillas, V. Guerschais, H. Le Bozec, A. Boucekkine, C. Latouche, *J. Organomet. Chem.*, 2014, **751**, 568–572.