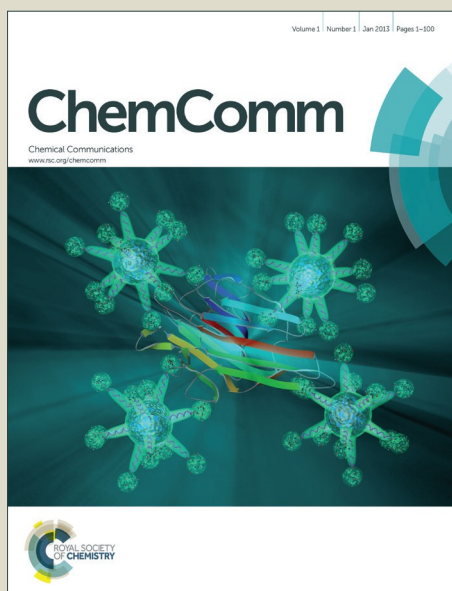


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4D- π -1A Type β -Substituted Zn^{II}-Porphyrins: Ideal Green Sensitizers for Building-Integrated Photovoltaics

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Two novel green β -substituted Zn^{II}-porphyrins, G1 and G2 based on 4D- π -1A type substitution pattern have been synthesized. Their enhanced *push-pull* character, by reduction of H-L energy gaps, promotes broadening and red-shifting of absorption bands. The effective synthetic pathway and the remarkable spectroscopic properties make G2 ideal for BIPV application.

The collective interest on renewable energy resources, because of the steady increase of global warming ascribed to the green-house gases from fossil fuels, has given light to photovoltaics as a sustainable energy supply. Dye-Sensitized Solar Cells (DSSCs) have received considerable attention as a promising alternative to the traditional silicon-based solar cells achieving excellent photon-to-current conversion efficiencies.¹⁻³ The cheap and transparent TiO₂ semiconductor⁴ makes DSSCs very intriguing for specific application in Building Integrated Photovoltaics (BIPV),⁵⁻⁷ especially in assembling see-through photovoltaic glass windows.⁸⁻¹⁰ In future scope of DSSC for BIPV application desirable colourful PV glazing, from green to blue,¹¹ should be obtained to meet aesthetic requirements of building façades and the cost reduction must be considered for a mass scale production.^{8-10, 12} Unlike organic sensitizers, which usually display orange/red colour, porphyrin dyes could provide more attractive greenish devices. Hereto, fine-tuned porphyrin-sensitized solar cells have reached 13% conversion efficiency in presence of Co^{II/III} redox mediator by using SM315³ dye belonging to the series of 5,15-meso-substituted Zn^{II}-porphyrins. Such a series is known to show excellent photoelectrochemical characteristics and good near infrared (NIR) absorptions;^{13, 14} nevertheless it needs a very demanding and laborious synthetic pathway. Furthermore, the presence of cobalt redox shuttle forces the introduction of additional

bulky alkoxy chains in the dye structure to suppress the fast recombination processes.¹⁵ For these reasons the industrial scale-up of this class of porphyrin dyes cannot be taken into consideration for a practical application on BIPV. Conversely, β -substituted porphyrins, based on a highly symmetric meso-tetraarylsubstituted core, easily obtained by one-pot cyclization reactions between appropriate aryl-aldehydes and pyrrole, appear to be synthetically more convenient for a mass scale production necessary to sensitize large decorative DSSC modules integrated in PV windows of building façades. Consequently, they have recently received renewed interest¹⁶⁻²⁶ from the scientific community which led to an improvement of the overall synthetic yields up to two-fold, superior to those earlier reported,²⁷ by optimising both functionalization^{28, 29} and substitution³⁰ processes on β -pyrrolic position. Their native bulky structure can also provide a significant shielding effect onto TiO₂ surface against charge recombination when compared to the 5,15-meso-substituted analogues.¹⁸ Here we propose to combine the key features of meso- and β -substituted porphyrins to guarantee ideal characteristics for BIPV application designing green sensitizers accessible by straightforward and efficient synthetic pathways and featured by extended electron absorption across the visible spectrum. A rational engineering of the porphyrin structure affects on its electronic properties and, thus, the HOMO and LUMO energy levels can be properly tuned.³¹ As a consequence, dyes with increased *push-pull* character can be synthesized to gain ideal spectroscopic and photoelectrochemical characteristics. The introduction of multiple donating aryl substituents in the meso

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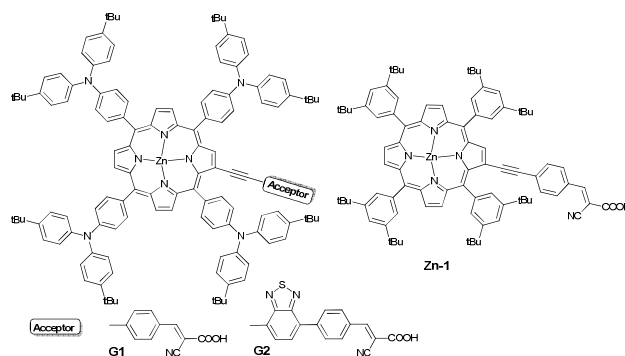


Chart 1: Molecular Structures of Zn-1, G1 and G2

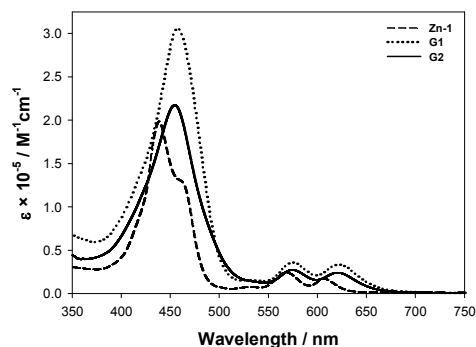


Figure 1: Absorption Spectra of Zn-1, G1 and G2 in THF Solution.

positions of porphyrin dyes was previously evidenced to have significant electronic effects on HOMO levels.^{32–38} This produces broadening of B band, intensification of Q bands and red-shifting of both absorption peaks thus improving the light-harvesting properties of the dye both in the visible and NIR regions.^{39, 40} However, in the previous approaches, the obtained dyes were highly asymmetric making their synthetic strategy poorly effective.⁴¹

Hence, two new β -substituted porphyrinic dyes, G1 and G2 (Chart 1) have been synthesized by introducing four electron-donating groups in meso position and an electron-withdrawing unit in one of the β -pyrrolic positions. Herein, bis(4-tert-butylphenyl)aniline, as a bulky donor substituent, has been chosen both to induce a significant electronic effect on the HOMO levels and to reduce, simultaneously, the recombination rate onto TiO₂ semiconductor. The ethynylphenyl-cyanoacrylic acid group, as an acceptor and anchoring pendant, was originally selected to obtain the G1 dye while a benzotriazole moiety (BTD) was further inserted into the β -pyrrolic substituent providing the G2 dye. The latter was rationally designed to increase the electron-withdrawing ability of the acceptor unit which affects on LUMO levels and, simultaneously, to extend the anchoring pendant in order to strengthen the binding of the dye onto the semiconductor. To the best of our knowledge, the structural arrangement of the new reported β -substituted porphyrinic dyes was never proposed, thus, for a better discussion and simplicity hereafter this donor-acceptor pattern will be referred to as 4D- π -1A type.

G1 and G2 were easily obtained by multiple Buchwald–Hartwig aminations of the Zn^{II}-tetra(4-bromophenyl)porphyrin followed, first, by a bromination step on β -pyrrolic position and then by a substitution step via microwave-enhanced Sonogashira coupling³⁰ to introduce the acceptor unit, as fully described in ESI. For comparison, the Zn-1 reference dye (Chart 1), lacking of amino groups, was synthesized, as described elsewhere.³⁰ Cyclic voltammetry measurements in DMF were carried out with the aim to determine how the redox potentials of the dyes are influenced by the nature of substituents. The HOMO and LUMO energy levels and the corresponding energy gaps (H-L gaps) in DMF, electrochemically determined and computed at the B3LYP/6-311G(d) level, are reported in Table 1. It turns out that the four arylamino donor groups in meso position induce a significant destabilisation of the HOMO

energy levels. The 4D- π -1A type dyes, in fact, exhibit a first oxidation wave at a less positive potential (Tab. S2), resulting in HOMO levels located at higher energy, -5.04 eV and -5.03 eV respectively for G1 and G2, when compared with Zn-1 (-5.12 eV).

Table 1: Electrochemical and Computational HOMO and LUMO energies of Zn-1, G1 and G2 in DMF Solution.

	Electrochemical Data [eV]			Computed data [eV]		
	E_{LUMO}	E_{HOMO}	ΔE_{H-L}	E_{LUMO}	E_{HOMO}	ΔE_{H-L}
Zn-1	-3.11	-5.12	2.01	-3.01	-5.30	2.30
G1	-3.10	-5.04	1.94	-2.98	-5.06	2.08
G2	-3.21	-5.03	1.82	-3.14	-5.06	1.92

This trend is accurately reproduced by DFT calculations (Tab. 1) and by the electronic distributions for the HOMOs of 4D- π -1A type porphyrins (Fig. S4 and S5) delocalized on the four arylamino groups rather than only on the porphyrinic core, as in the case of Zn-1 (Fig. S3). A significant stabilisation of the LUMO energy level of G2 (-3.21 eV), due to the presence of the BTD moiety in the acceptor unit, is in agreement with the less negative first reduction wave potential (Tab. S2) and it is also confirmed by the LUMOs delocalization on the more extended β -pyrrolic substituent, as shown by electronic distributions for the unoccupied molecular orbitals (Fig S3, S4 and S5). As a consequence, the trend of the H-L energy gaps, correlated with the electron-donating and electron-withdrawing ability of the substituents, is Zn-1 (2.01 eV) > G1 (1.94 eV) > G2 (1.82 eV) evidencing a marked increase of the *push-pull* character in the Zn^{II}-porphyrins with the 4D- π -1A substitution pattern. This affects the spectroscopic properties of the G1 and G2 dyes resulting in red-shifting and concomitant broadening of both B and Q bands as observed in their absorption spectra in THF solution (Fig. 1) and in the corresponding spectroscopic data and the computed excitation energies reported in Table S1. In particular, B and Q2 absorption bands of G1 (respectively 457 nm and 621 nm) and G2 (454 nm and 620 nm) are red-shifted compared to those of Zn-1 (438 nm and 608 nm), while slight differences are shown for Q1 absorption bands (568 nm, 575 nm and 574 nm for Zn-1, G1 and G2 respectively). In accordance with the bathochromic shift of Q absorption bands a red-shifted fluorescence emission was also observed for G1 and G2 compared to Zn-1 (see ESI for more information).

Different solvents, soaking time and dye/chenodeoxycholic acid (CDCA) ratio, have been tested to optimise the DSSC performances using I⁻/I₃⁻ as redox mediator in the electrolyte. The best conversions, for all three dyes, have been generally obtained using 0.2 mM dye solutions in CH₂Cl₂ and 20 hours of loading time. The presence of ten equivalents of CDCA was found to be very beneficial in the case of G2, while it was negative for G1 and Zn-1. This is probably ascribed to the more extended BTD-based anchoring pendant of G2 which could guarantee a most efficient binding onto TiO₂, thereby resisting to a greater extent to the competition with CDCA during the loading step. Photon-to-current conversion efficiency (IPCE) spectra and current density-to-voltage characteristics (J-V curves under illumination and in the dark) are reported in Figure 2, while the related photovoltaic characteristics are listed in Table 2 and refer to the best results obtained in a group of at least three devices for each configuration

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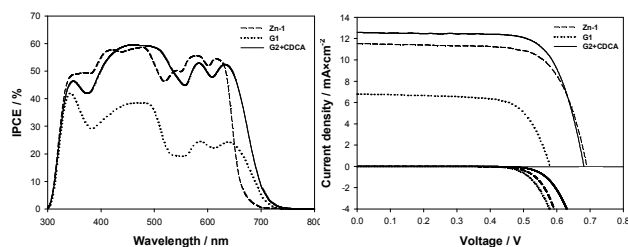


Figure 1: a) IPCE plots of Zn-1, G1 and G2 in the best conditions (left); b) J-V characteristics under illumination and in dark conditions (right).

(complete results are listed in Table S3). 6.22% light-to-current conversion efficiency (η) was achieved for G2+CDCA sensitized DSSC with mask and 8.79% without. These values are remarkable by considering that up to now the best performance, achieved by a β -substituted porphyrin sensitized solar cell, reached 7.1% efficiency⁴² (with or without a mask was not declared). Surprisingly, the Zn-1 sensitized DSSC ($\eta = 5.62\%$) better performed than the G1 based one ($\eta = 2.72\%$), despite the narrower H-L energy gap and the wider electronic absorptions across the visible spectrum of G1 dye. IPCE spectra of the aforementioned DSSCs confirm this trend. G2 sensitized DSSC exhibits significant IPCE% values (up to 60%) over a very broad spectral range (300–700 nm) while much lower values of IPCE% are shown by G1 based DSSC (<40%) compared to the Zn-1 based one (around 60%), although a photocurrent over 700 nm is observed for both 4D- π -1A type dyes. The Zn-1 sensitized DSSC shows, in fact, good IPCE% values only up to 620 nm due to the limited *push-pull* character by lacking of amino-groups. These differences can be attributed by reason of the short anchoring substituent in G1 dye with respect to the bulky amino-groups surrounding the core which hamper an adequate loading of the dye onto the TiO₂ surface. In Zn-1 and G2, otherwise, the anchoring chain protrudes by about 5 Å with respect to the surface enveloped by the four aryl amino groups (Fig. S3 and S5) favouring a superior dye loading. A spectrophotometric evaluation (Fig. S10) of the dye loading capacity on transparent thin TiO₂ layers was carried out to corroborate such assumption. Surface concentrations (Γ) of $3.56 \cdot 10^{-8}$ mol/cm² and $3.76 \cdot 10^{-8}$ mol/cm² were found for Zn-1 and G2 respectively, while a concentration of $1.94 \cdot 10^{-8}$ mol/cm² was found for G1 (Tab. S4), in agreement with expectations. Furthermore, an increase of the recombination rate at the surface of G1 sensitized DSSC is observed by the anticipated current onset (by ca. 50 mV compared with G2) exhibited by the J-V curves in the dark condition (Fig. 2b). Accordingly, the shorter anchoring unit of G1 dye could promote the approaching of the amino groups to the semiconductor surface favouring a back electron transfer by the overlap of the electronic hole at the periphery of the porphyrin ring and the injected electrons in the semiconductor. Alternatively, a more facile recombination kinetic could be promoted by the I₃⁻ approach onto TiO₂. Comparative photophysical studies about dynamics of the new dyes at the TiO₂/electrolyte interface are currently underway to elucidate the possible reasons of their different behaviours. Finally electrochemical impedance spectroscopy (EIS) investigation has confirmed the observations gained by J-V curves. Higher values of measured capacitance (C_{meas}), charge

transfer resistance (R_{ct}) and apparent electron lifetime (τ) were found (Fig. S9) for Zn-1 and G2 sensitized photoanodes with respect to those G1 sensitized.

Table 2: Photovoltaic Characteristics of the DSSC based on Zn-1, G1 and G2 in their Best Conditions under standard AM 1.5 simulated solar illumination.

DYE	mask	η	FF	Voc (V)	Jsc (mA/cm ²)
Zn-1	-	8.07	65.5	0.719	17.13
	•	5.62	70.6	0.690	11.53
Zn-1+CDCA	-	6.26	70.5	0.664	13.37
	•	4.64	73.9	0.643	9.77
G1	-	4.12	64.5	0.608	10.50
	•	2.72	69.4	0.580	6.77
G1+CDCA	-	1.49	60.9	0.571	4.29
	•	1.19	68.2	0.558	3.13
G2	-	5.97	62.7	0.670	14.23
	•	4.37	68.0	0.656	9.87
G2+CDCA	-	8.79	69.8	0.700	17.98
	•	6.22	72.6	0.681	12.58

The value of C_{meas} is related to the difference between the electron Fermi level (E_{Fn}) and the conduction band (E_{cb}) of TiO₂.⁴³ The displacement of capacitance plots (Fig. S9) indicates that the conduction band of G1 and G2 sensitized photoanodes does not present a relevant shift, so that the recombination resistance, R_{ct} , can be treated on the basis of a similar number of electrons.⁴⁴ G2 definitely exhibits a higher value of R_{ct} (Fig. S9) compared to G1, justifying the higher value of Voc. This can be attributed to the positive effect of the longer BTD-based anchoring unit in G2, which allows the amino groups to move away from TiO₂ surface, unlike G1 (vide supra). On the contrary, the reference Zn-1 dye, lacking the amino groups, produces different values of the Fermi level and conduction band, resulting in higher C_{meas} values. However, Zn-1 and G2 show similar values of R_{ct} , but, as a result of a more significant C_{meas} , the values of τ are slightly higher for Zn-1. Hence, G2 and Zn-1 show higher τ values in perfect accordance with the trend detected for photovoltaic performances in comparison with G1.

In conclusion we have designed and synthesized two Zn^{II}-porphyrin sensitizers, G1 and G2, featured by a novel 4D- π -1A type substitution pattern showing four bulky electron-donating substituents in *meso* position and a β -pyrrolic electron-withdrawing pendant. This substitution pattern confers to the dyes the attractive spectroscopical characteristics of the *push-pull* meso-disubstituted porphyrins guarantying a concomitant effective and straightforward synthetic pathway typical of the β -substituted porphyrins. Thus, our approach results a viable and robust method to obtain green and cost-effective sensitizers meeting the esthetical and economical requirements necessary for a mass scale production in BIPV industrial application. A rational design and a fine tailoring of G2 molecular structure provided also a narrower H-L energy gap resulting in an enhanced *push-pull* character. This promoted broadening and red-shifting of the absorption bands resulting in an improved light-harvesting ability of the dye across the visible spectrum. Moreover G2 reached remarkable light-to-power conversion efficiency (8.79% without mask) by a typical Γ/I_3^- based DSSC leaving plenty of room for further improvements by a fine-tuning of the device fabrication conditions.

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Notes and references

- Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li and P. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 3799-3802.
- K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-i. Fujisawa and M. Hanaya, *Chem. Commun.*, 2015, **51**, 15894-15897.
- S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, K. Nazeeruddin, M. Grätzel, *Nat Chem*, 2014, **6**, 242-247.
- B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737-740.
- B. Parida, S. Iniyan and R. Goic, *Renewable Sustainable Energy Rev.*, 2011, **15**, 1625-1636.
- B. Petter Jelle, C. Breivik and H. Drolsum Røkenes, *Sol. Energy Mater. Sol. Cells*, 2012, **100**, 69-96.
- A. Reale, L. Cinà, A. Malatesta, R. De Marco, T. M. Brown and A. Di Carlo, *Energy Technol.*, 2014, **2**, 531-541.
- M. Saifullah, J. Gwak and J. H. Yun, *J. Mater. Chem. A*, 2016, **4**, 8512-8540.
- S. Yoon, S. Tak, J. Kim, Y. Jun, K. Kang and J. Park, *Build. Environ.*, 2011, **46**, 1899-1904.
- A. Hinsch, H. Brandt, W. Veurman, S. Hemming, M. Nittel, U. Würfel, P. Putyra, C. Lang-Koetz, M. Stabe, S. Beucker and K. Fichter, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 820-824.
- W. Zhang, M. Anaya, G. Lozano, M. E. Calvo, M. B. Johnston, H. Miguez and H. J. Snaith, *Nano Lett.*, 2015, **15**, 1698-1702.
- Y.-C. Liu, H.-H. Chou, F.-Y. Ho, H.-J. Wei, T.-C. Wei and C.-Y. Yeh, *J. Mater. Chem. A*, 2016, **4**, 11878-11887.
- L.-L. Li and E. W.-G. Diau, *Chem. Soc. Rev.*, 2013, **42**, 291-304.
- J.-W. Shiu, Y.-C. Chang, C.-Y. Chan, H.-P. Wu, H.-Y. Hsu, C.-L. Wang, C.-Y. Lin and E. W.-G. Diau, *J. Mater. Chem. A*, 2015, **3**, 1417-1420.
- S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo and A. Hagfeldt, *J. Am. Chem. Soc.*, 2010, **132**, 16714-16724.
- T. Higashino and H. Imahori, *Dalton Trans.*, 2015, **44**, 448-463.
- G. Di Carlo, A. Orbelli Biroli, F. Tessore, M. Pizzotti, P. R. Mussini, A. Amat, F. De Angelis, A. Abbotto, V. Trifiletti and R. Ruffo, *J. Phys. Chem. C*, 2014, **118**, 7307-7320.
- G. Di Carlo, S. Caramori, V. Trifiletti, R. Giannuzzi, L. De Marco, M. Pizzotti, A. Orbelli Biroli, F. Tessore, R. Argazzi and C. A. Bignozzi, *ACS Appl. Mater. Interfaces*, 2014, **6**, 15841-15852.
- A. Orbelli Biroli, F. Tessore, V. Vece, G. Di Carlo, P. R. Mussini, V. Trifiletti, L. De Marco, R. Giannuzzi, M. Manca and M. Pizzotti, *J. Mater. Chem. A*, 2015, **3**, 2954-2959.
- G. Magnano, D. Marinotto, M. P. Cipolla, V. Trifiletti, A. Listorti, P. R. Mussini, G. Di Carlo, F. Tessore, M. Manca, A. Orbelli Biroli and M. Pizzotti, *PCCP*, 2016, **18**, 9577-9585.
- T. Sakurada, Y. Arai and H. Segawa, *RSC Adv.*, 2014, **4**, 13201-13204.
- M. Ishida, D. Hwang, Z. Zhang, Y. J. Choi, J. Oh, V. M. Lynch, D. Y. Kim, J. L. Sessler and D. Kim, *ChemSusChem*, 2015, **8**, 2967-2977.
- J. Chen, K.-L. Li, Y. Guo, C. Liu, C.-C. Guo and Q.-Y. Chen, *RSC Adv.*, 2013, **3**, 8227-8231.
- M. Ishida, D. Hwang, Y. B. Koo, J. Sung, D. Y. Kim, J. L. Sessler and D. Kim, *Chem. Commun.*, 2013, **49**, 9164-9166.
- H. van der Salm, P. Wagner, K. Wagner, D. L. Officer, G. G. Wallace and K. C. Gordon, *Chem. - Eur. J.*, 2015, **21**, 15622-15632.
- S. Eu, S. Hayashi, T. Umeyama, Y. Matano, Y. Araki and H. Imahori, *J. Phys. Chem. C*, 2008, **112**, 4396-4405.
- C.-W. Lee, H.-P. Lu, C.-M. Lan, Y.-L. Huang, Y.-R. Liang, W.-N. Yen, Y.-C. Liu, Y.-S. Lin, E. W.-G. Diau and C.-Y. Yeh, *Chem. - Eur. J.*, 2009, **15**, 1403-1412.
- G. Di Carlo, A. Orbelli Biroli, F. Tessore, S. Rizzato, A. Forni, G. Magnano and M. Pizzotti, *J. Org. Chem.*, 2015, **80**, 4973-4980.
- A. Fermi, M. Locritani, G. Di Carlo, M. Pizzotti, S. Caramori, Y. Yu, B. A. Korgel, G. Bergamini and P. Ceroni, *Faraday Discuss.*, 2015, **185**, 481-495.
- G. Di Carlo, A. Orbelli Biroli, M. Pizzotti, F. Tessore, V. Trifiletti, R. Ruffo, A. Abbotto, A. Amat, F. De Angelis and P. R. Mussini, *Chem. - Eur. J.*, 2013, **19**, 10723-10740.
- P. R. Mussini, A. Orbelli Biroli, F. Tessore, M. Pizzotti, C. Biaggi, G. Di Carlo, M. G. Lobello and F. De Angelis, *Electrochim. Acta*, 2012, **85**, 509-523.
- E. C. Ojadi, H. Linschitz, M. Gouterman, R. I. Walter, J. S. Lindsey, R. W. Wagner, P. Droupadi and W. Wang, *J. Phys. Chem.*, 1993, **97**, 13192-13197.
- J. N. Clifford, G. Yahioglu, L. R. Milgrom and J. R. Durrant, *Chem. Commun.*, 2002, 1260-1261.
- C.-W. Huang, K. Yuan Chiu and S.-H. Cheng, *Dalton Trans.*, 2005, 2417-2422.
- Z. Zhang, R. M. Edkins, J. Nitsch, K. Fucke, A. Eichhorn, A. Steffen, Y. Wang and T. B. Marder, *Chem. - Eur. J.*, 2015, **21**, 177-190.
- S. Karthikeyan and J. Y. Lee, *J. Phys. Chem. A*, 2013, **117**, 10973-10979.
- H. Imahori, Y. Matsubara, H. Iijima, T. Umeyama, Y. Matano, S. Ito, M. Niemi, N. V. Tkachenko and H. Lemmetyinen, *J. Phys. Chem. C*, 2010, **114**, 10656-10665.
- R. B. Ambre, S. B. Mane, G.-F. Chang and C.-H. Hung, *ACS Appl. Mater. Interfaces*, 2015, **7**, 1879-1891.
- C.-Y. Huang, C.-Y. Hsu, L.-Y. Yang, C.-J. Lee, T.-F. Yang, C.-C. Hsu, C.-H. Ke and Y. O. Su, *Eur. J. Inorg. Chem.*, 2012, **2012**, 1038-1047.
- G. Y. Gao, Y. Chen and X. P. Zhang, *J. Org. Chem.*, 2003, **68**, 6215-6221.
- K. Kurotobi, Y. Toude, K. Kawamoto, Y. Fujimori, S. Ito, P. Chabera, V. Sundström and H. Imahori, *Chem. - Eur. J.*, 2013, **19**, 17075-17081.
- W. M. Campbell, K. W. Jolley, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. Schmidt-Mende, M. K. Nazeeruddin, Q. Wang, M. Grätzel and D. L. Officer, *J. Phys. Chem. C*, 2007, **111**, 11760-11762.
- J. Bisquert, *PCCP*, 2003, **5**, 5360-5364.
- J. Bisquert, F. Fabregat-Santiago, I. Mora-Seró, G. Garcia-Belmonte and S. Giménez, *J. Phys. Chem. C*, 2009, **113**, 17278-17290.