



Synthesis and spectral properties of ruthenium(II) complexes based on 2,2'-bipyridines modified by a perylene chromophore



Koichi Kodama, Akinori Kobayashi, Takuji Hirose*

Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan

ARTICLE INFO

Article history:

Received 8 May 2013

Revised 23 July 2013

Accepted 29 July 2013

Available online 3 August 2013

Keywords:

Perylene

Ruthenium complex

2,2'-Bipyridine

Ligand design

Absorption spectra

ABSTRACT

Five new 2,2'-bipyridines functionalized with a perylene or a perylenediimide moiety were synthesized and the corresponding heteroleptic ruthenium(II) complexes ($[\text{Ru}(\text{bpy})_2(\text{L})](\text{PF}_6)_2$; bpy = 2,2'-bipyridyl, L = perylene-substituted bpy ligand) were prepared. The UV-vis spectra of the ruthenium(II) complexes showed red-shifted and intense absorption bands derived from the conjugated structure of the new ligands.

© 2013 Elsevier Ltd. All rights reserved.

Transition metal complexes with multidentate *N*-heterocyclic ligands have been attracting a great deal of interest because of their wide variety of applications in dye-sensitized solar cells (DSSCs),¹ organic light-emitting diodes,² nonlinear optical materials,³ and so on. To develop more potent materials, the complexes should efficiently absorb visible light through metal-to-ligand charge transfer (MLCT) transition. Because the physical properties of the complexes can be easily controlled by structural modification of the ligands, various types of ligands have been reported to improve the absorption properties.⁴ In particular, bidentate ligands based on 2,2'-bipyridines (bpy) are some of the most intensely studied class of compounds because of their synthetic accessibility and reliable coordination ability. A promising method to enhance the absorption property is extension of the π -conjugated system of ligands. Many bpy-based ligands covalently linked with aromatic moieties to extend π -conjugation have been reported to achieve efficient absorption of visible light as well as the longer excited state lifetime of their metal complexes.⁵ For example, it was reported that ruthenium(II) complexes consisting of bpy-pyrene-conjugated ligands stabilized the excited state sufficiently enough to promote bimolecular electron-transfer reactions.^{5e,f}

Perylene and perylenediimides (PDIs) are photochemically stable chromophores with large π -conjugated systems and rigid planar structures. Owing to these advantages, they have been widely applied to fluorescent sensors, organic field-effect

transistors, and so on.⁶ Therefore, the perylene chromophore is a candidate to improve the optical properties of the bpy-based ligands and provide a red-shift of MLCT absorption band and an increased molar extinction coefficient of the metal complexes. Because 2,2'-bipyridines equipped with perylene moieties have been rarely reported,⁷ we describe the synthesis of five novel 2,2'-bipyridines functionalized with a perylene moiety (**L1–L5**, Fig. 1) and their heteroleptic ruthenium(II) complexes, $[\text{Ru}(\text{bpy})_2(\text{L})](\text{PF}_6)_2$. In addition, we compare the characteristics of the Ru complexes on the basis of their photophysical properties.

Synthesis of ligands **L1** and **L2** containing PDI units and derivatization to **L3** containing a diamine moiety are shown in Scheme 1. Both **L1** and **L2** are unsymmetrical PDIs with different substituents on each imide nitrogen atom and have been synthesized according to the two established strategies. According to the literature, tetrabromo-substituted *N,N'*-dihexyl-PDI **3** was prepared from commercially available perylene-3,4,9,10-tetracarboxylic dianhydride **1**.⁸ Partial hydrolysis of **3** under basic conditions in an aqueous *t*-BuOH solution afforded the mixed imide-anhydride **4**; subsequent imidation of the precursor **4** with 4-amino-2,2'-bipyridine **7**⁹ afforded **L1** in moderate yield.¹⁰ In order to improve the solubility of the ligand, a longer alkyl chain was introduced on the imide group of **L2**. Unsymmetrical PDI **L2** was obtained in good yield by partial hydrolysis of **1** followed by successive imidation with two different amines, octadecylamine and **7**.¹¹ Diamine ligand **L3** was synthesized by hydride reduction of diimide **L2** with $\text{LiAlH}_4/\text{AlCl}_3$ mixed system, which was applied to reduce *N,N'*-dibutyl-PDI derivatives to the corresponding diamines.¹²

* Corresponding author. Tel./fax: +81 48 858 9548.

E-mail address: hirose@apc.saitama-u.ac.jp (T. Hirose).

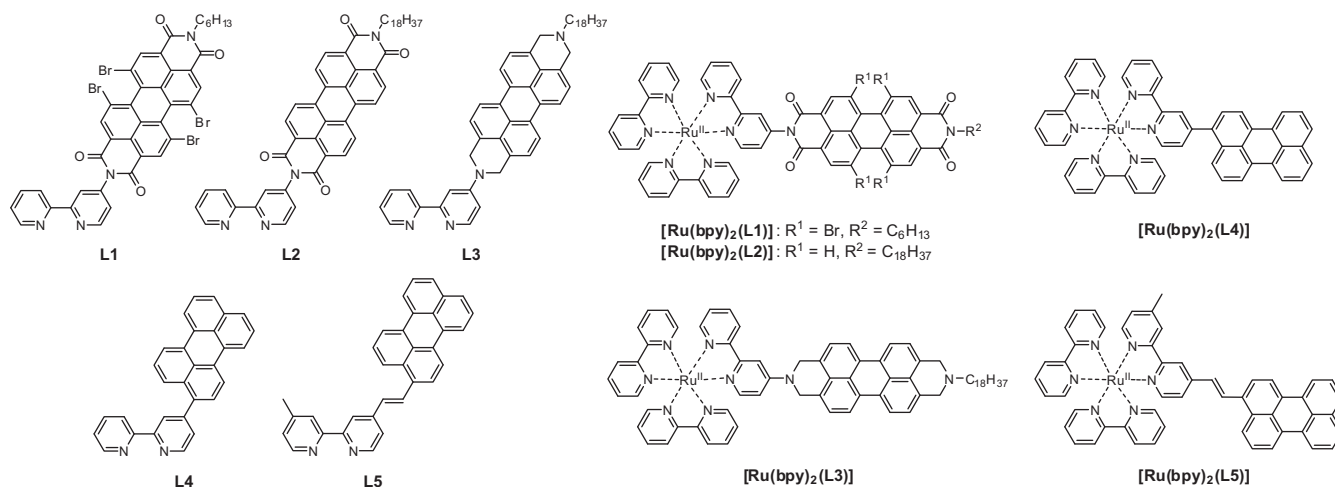
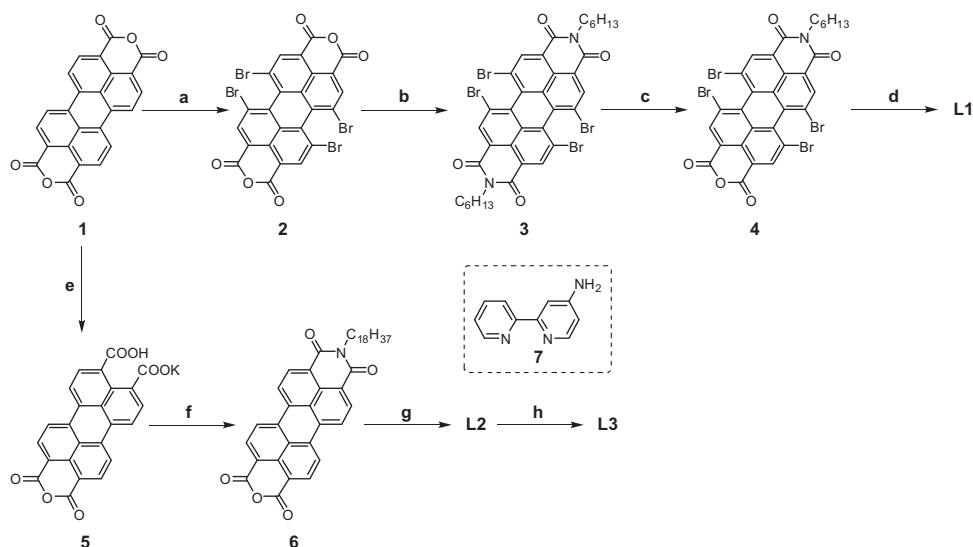


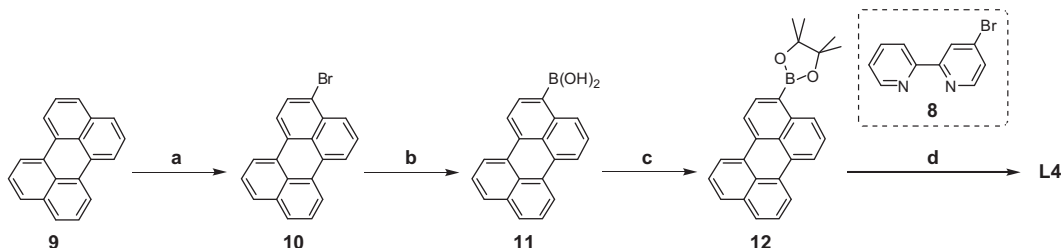
Figure 1. Structures of perylene-functionalized 2,2'-bipyridines (**L1–L5**) and their ruthenium(II) complexes prepared in this study.



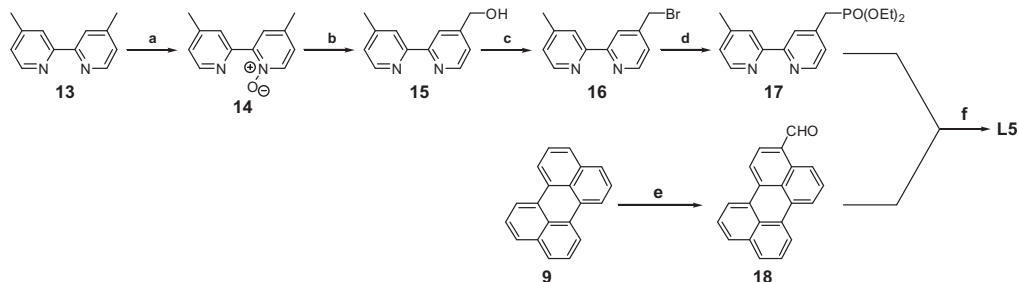
Scheme 1. Synthetic routes to the perylene-functionalized 2,2'-bipyridine ligands (**L1–L3**). Reagents and conditions: (a) Br₂, cat. I₂, fuming H₂SO₄, concd H₂SO₄, Δ; (b) C₆H₁₃NH₂, C₂H₅COOH, Δ (69% from **1**); (c) (i) KOH, *t*-BuOH, Δ; (ii) 2N HCl (56%); (d) compound **7**, cat. DMAP, dry quinoline, Δ (75%); (e) KOH, AcOH/H₂O, Δ; (f) C₁₈H₃₇NH₂, *n*-PrOH/H₂O, Δ (67% from **1**); (g) compound **7**, cat. DMAP, quinoline, Δ (75%); (h) AlCl₃, LiAlH₄, dry THF, 0 °C to reflux temperature (41%).

Two remaining ligands **L4** and **L5** were synthesized according to Schemes 2 and 3, respectively. The new ligand **L4** has a simple molecular structure, where perylene is directly attached to the bpy unit, and was expected to expand the absorption range of the visible light. It was successfully obtained by coupling of 4-bromo-2,2'-bipyridine **8**¹³ and perylene boronic ester **12**¹⁴ in high yield (86%) under the usual Suzuki–Miyaura coupling conditions.

In order to further extend the π -conjugated system of ligand **L4**, **L5** was designed as the perylenyl group that was replaced with a perylenylvinyl moiety and introduced into the bpy unit. The synthesis of **L5** was carried out according to the Horner–Wadsworth–Emmons reaction, which is known to afford *E*-alkene selectively. One required precursor, 3-formylperylene **18**, was prepared in good yield from **9** by the Vilsmeier–Haack reaction.¹⁵



Scheme 2. Synthetic routes to the perylene-functionalized 2,2'-bipyridine ligand (**L4**). Reagents and conditions: (a) NBS, dry THF, rt (83%); (b) (i) *n*-BuLi, dry THF, –78 °C; (ii) B(OMe)₃, –78 °C to rt; (c) pinacol, MS 3A, dry toluene Δ (80% from **10**); (d) compound **8**, cat. Pd(PPh₃)₄, 2 N K₂CO₃, EtOH/toluene, Δ (86%).



Scheme 3. Synthetic routes to the perylene-functionalized 2,2'-bipyridine ligand (**L5**). Reagents and conditions: (a) mCPBA, CHCl₃, 0 °C to rt (75%); (b) (i) Ac₂O, Δ; (ii) 10% NaOH, Δ (46%); (c) 48% HBr, concd H₂SO₄, Δ (91%); (d) P(OEt)₃, CHCl₃, Δ (42%); (e) DMF, POCl₃, dry *o*-dichlorobenzene, Δ (82%); (f) *t*-BuOK, dry THF, rt (94%).

The other precursor, phosphonate **17**, was a known compound and synthesized in four steps from 4,4'-dimethyl-2,2'-bipyridine **13** by oxidation, esterification and followed by hydrolysis, bromination, and the subsequent Michaelis–Arbuzov reaction with triethylphosphite.^{5e,16} Finally, **L5** was obtained in high yield (94%) from **17** and **18** in the presence of *t*-BuOK in tetrahydrofuran (THF) solution. The five heteroleptic ruthenium(II) complexes [Ru(bpy)₂(**L**)](PF₆)₂ consisting of one perylene-containing **L** and two 2,2'-bipyridine molecules were prepared by mixing Ru(bpy)₂Cl₂·2H₂O and **L**, followed by anion exchange by the addition of saturated KPF₆ solution. The obtained ruthenium(II) complexes were characterized by ESI-MS spectroscopy.

The UV–vis absorption spectra of ruthenium(II) complexes in dimethylformamide (DMF) solution are shown in Figure 2. Absorption maxima together with molar extinction coefficients are summarized in Table 1. The spectra of [Ru(bpy)₂(**L1**)] and [Ru(bpy)₂(**L2**)] complexes show a similar profile and three absorption maxima appeared at approximately 450, 500, and 530 nm. These maxima are characteristic for PDI-localized π–π* transition while some overlap of MLCT transitions is present between 420 and 500 nm.^{6e,17} A slight red-shift of the absorption of [Ru(bpy)₂(**L1**)] compared with [Ru(bpy)₂(**L2**)] would result from the resonance effect of four bromo substituents at the bay positions of PDI in **L1**.¹⁸ The complex [Ru(bpy)₂(**L3**)] with two amino groups in the ligand showed a broad absorption peak with two maxima at 431 and 457 nm and a shoulder peak at 520 nm. The two higher energy bands were assigned to π–π* transitions of **L3** while the broad absorption and the shoulder peak can be attributed to a spin-forbidden MLCT transition. In contrast to the above three complexes, the complex [Ru(bpy)₂(**L4**)] showed one broad absorption peak with a maximum at 453 nm. It was suggested that MLCT transition as well as π–π* transition of the perylene moiety of **L4**

Table 1

UV–vis absorption and emission data of the Ru(II) complexes (1.0 × 10⁻⁵ M)

Ru complex	λ _{abs} , nm (ε, M ⁻¹ cm ⁻¹)	λ _{em} , nm
[Ru(bpy) ₂ (L1)](PF ₆) ₂	441(41,000), 500 (54,000), 533 (71,000)	569
[Ru(bpy) ₂ (L2)](PF ₆) ₂	461 (41,000), 492 (51,000), 528 (62,000)	567
[Ru(bpy) ₂ (L3)](PF ₆) ₂	431 (37,000), 457 (44,000), 520 (26,000)	583, 637
[Ru(bpy) ₂ (L4)](PF ₆) ₂	453 (44,000)	469, 495
[Ru(bpy) ₂ (L5)](PF ₆) ₂	488 (60,000)	538
[Ru(bpy) ₃](PF ₆) ₂	426 (26,500), 454 (33,100)	510, 611

contributed to the absorption. Although the molar extinction coefficient was increased compared with that of [Ru(bpy)₃], it was not clear whether the π-conjugated system in **L4** was extended by the directly coupled perylene moiety with a bpy unit. Such an influence by the extended π-conjugation of the bpy-based ligands was clearly observed for the complex [Ru(bpy)₂(**L5**)], which showed a broad and intense absorption peak at 400–600 nm. The significant red-shift of λ_{max}, approximately 30 nm, and higher absorptivity probably resulted from the introduction of a π-conjugated perylenylvinyl moiety in **L5**.

The emission spectra of ruthenium(II) complexes in CH₃CN are shown in Figure 3. All complexes exhibited emission at ambient temperature when the excitation wavelength was 450 nm (Table 1). The patterns of emission behavior of [Ru(bpy)₂(**L1**)] and [Ru(bpy)₂(**L2**)] were similar, and their emission maxima were 567–583 nm accompanied by a shoulder peak at 600–650 nm. As is the case in their absorption spectra, it is suggested these emissions are dominated by the PDI unit and partially contributed by MLCT transition.^{6c} Notably, the shoulder peak of [Ru(bpy)₂(**L3**)], which can be assigned to the MLCT emission, was red-shifted by approximately 30 nm compared with [Ru(bpy)₃] and other two

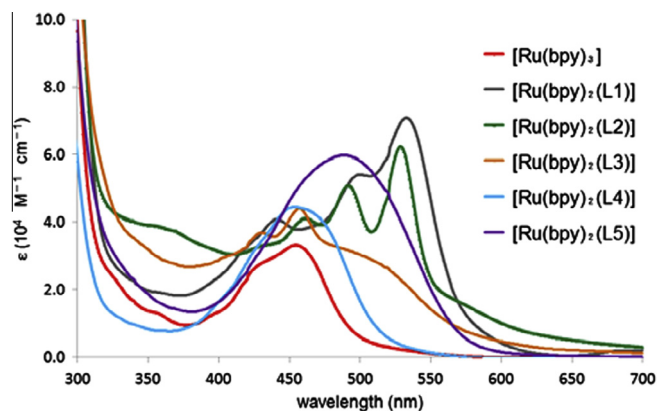


Figure 2. UV–vis absorption spectra of the Ru(II) complexes in DMF at room temperature with a concentration of 1.0 × 10⁻⁵ M.

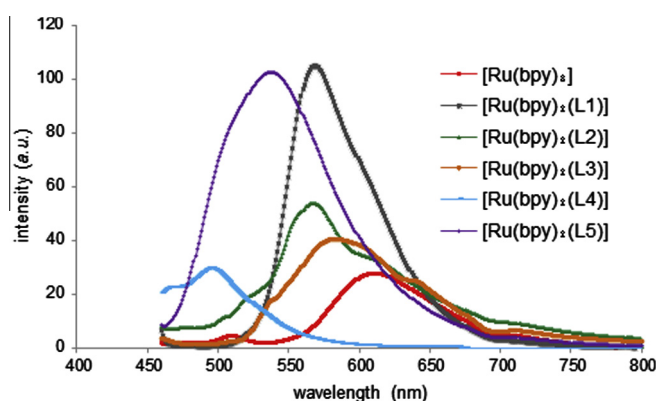


Figure 3. Emission spectra of the Ru(II) complexes in degassed CH₃CN at room temperature with a concentration of 1.0 × 10⁻⁵ M (λ_{ex} = 450 nm).

Table 2
Simulated UV–vis energy transitions of [Ru(bpy)₂(L4)] predicted by the TD-DFT method in DMF.

λ_{calcd} , nm	Oscillator strength (<i>f</i>)	Principal component of excitation
543	0.283	HOMO → LUMO, HOMO → LUMO+1
506	0.035	HOMO → LUMO+1, HOMO-1 → LUMO+1
457	0.650	HOMO → LUMO+3, HOMO-3 → LUMO
430	0.082	HOMO-2 → LUMO, HOMO-3 → LUMO+2
427	0.132	HOMO-3 → LUMO+1, HOMO-2 → LUMO+2

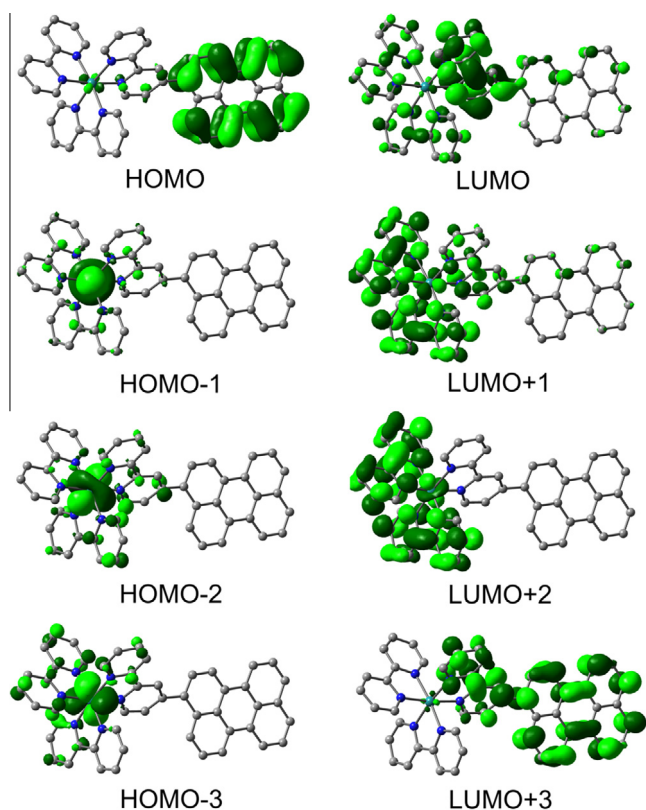


Figure 4. Schematic drawings of the selected frontier orbitals of [Ru(bpy)₂(L4)].

complexes. On the other hand, the complex [Ru(bpy)₂(L4)] showed an emission with maxima at 469 and 495 nm, which was similar to that of a known 2,2'-bipyridine derivative modified with the perylene moiety.^{7a} This result indicates that MLCT emission is completely quenched by the triplet excited state of L4, and intraligand emission from the perylene moiety is predominant.¹⁹ A similar situation was observed for the complex [Ru(bpy)₂(L5)] while the entire emission spectrum is red-shifted and the intensity was increased because of the extended π -conjugation system of the ligand.

To gain insight into the spectral properties of the complex, the absorption spectrum of [Ru(bpy)₂(L4)] was calculated using the TD-DFT method in DMF. The calculated energy and oscillator strength (*f*) are summarized in Table 2 and the predicted spectrum is shown in Figure S1. The simulated spectrum shows a broad absorption band and matched well with the experimental one. The most intense absorption band centered at $\lambda_{\text{calcd}} = 457$ nm resulted from the two transitions, HOMO to LUMO+3 and to a lesser extent, HOMO-3 to LUMO orbitals. From the visual inspection of the molecular orbitals depicted in Figure 4, the former bears intraligand π - π^* transition of L4 while the latter is mainly contributed

by the MLCT transition from Ru center to bipyridine moiety of L4. This result suggests that bpy moiety in L4 was distinguished from other two bpy ligands due to the conjugation with the perylene moiety.

In conclusion, we successfully synthesized five novel 2,2'-bipyridine-based ligands L1–L5 functionalized with a perylene moiety and also prepared a series of heteroleptic ruthenium(II) complexes [Ru(bpy)₂(L)](PF₆)₂. They showed different absorption and emission properties that depend on the structure of the perylene moiety and the size of the π -conjugation system. The insight presented here helps further design of metal complexes with broad and red-shifted absorption properties that can be utilized as sensitizers in DSSCs and photoredox reactions.

Supplementary data

Supplementary data (detailed experimental procedures, characterization of the materials, and simulated UV–vis spectrum) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.07.150>.

References and notes

- (a) Ardo, S.; Meyer, G. *J. Chem. Soc. Rev.* **2009**, *38*, 115–164; (b) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663.
- (a) Buda, M.; Kalyuzhny, G.; Bard, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 6090–6098; (b) Berner, D.; Klein, C.; Nazeeruddin, M. K.; Angelis, F. D.; Castellani, M.; Bugnon, P.; Scopelliti, R.; Zuppiroli, L.; Graetzel, M. *J. Mater. Chem.* **2006**, *16*, 4468–4474; (c) Slinker, J. D.; Rivnay, J.; Moskowitz, J. S.; Parker, J. B.; Bernhard, S.; Abruna, H. D.; Malliaras, G. G. *J. Mater. Chem.* **2007**, *17*, 2976–2988.
- (a) Maury, O.; Bozec, H. L. *Acc. Chem. Res.* **2005**, *38*, 691–704; (b) Coe, B. J.; Harris, J. A.; Bruntschwig, B. S.; Asselberghs, I.; Clays, K.; Garin, J.; Orduna, J. *J. Am. Chem. Soc.* **2005**, *127*, 13399–13410.
- (a) Vos, J. G.; Kelly, J. M. *Dalton Trans.* **2006**, 4869–4883; (b) Coe, B. J.; Harper, E. C.; Helliwell, M.; Ta, Y. T. *Polyhedron* **2011**, *30*, 1830–1841.
- (a) Simon, J. A.; Curry, S. L.; Schmehl, R. H.; Schatz, T. R.; Piotrowiak, P.; Jin, X.; Thummel, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 11012–11022; (b) Guerzo, A. D.; Leroy, S.; Fages, F.; Schmehl, R. H. *Inorg. Chem.* **2002**, *41*, 359–366; (c) Jiang, K.-J.; Masaki, N.; Xia, J.-B.; Noda, S.; Yanagida, S. *Chem. Commun.* **2006**, 2460–2462; (d) Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 10720–10728; (e) Gu, J.; Chen, J.; Schmehl, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 7338–7346; (f) Grusenmeyer, T. A.; Chen, J.; Jin, Y.; Nguyen, J.; Rack, J. J.; Schmehl, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 7497–7506.
- (a) Li, Y.; Zheng, H.; Li, Y.; Wang, S.; Wu, Z.; Liu, P.; Gao, Z.; Liu, H.; Zhu, D. *J. Org. Chem.* **2007**, *72*, 2878–2885; (b) Jung, C.; Ruthardt, N.; Lewis, R.; Michaelis, J.; Sodeik, B.; Nolde, F.; Peneva, K.; Müllen, K.; Bräuchle, C. *ChemPhysChem* **2009**, *10*, 180–190; (c) Langhals, H.; Obermeier, A.; Floredo, Y.; Zanelli, A.; Flamigni, L. *Chem. Eur. J.* **2009**, *15*, 12733–12744; (d) Jung, B. J.; Tremblay, N. J.; Yeh, M.-L.; Katz, H. E. *Chem. Mater.* **2011**, *23*, 568–582; (e) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, *76*, 2386–2407; (f) Céspedes-Guirao, F. J.; Ropero, A. B.; Font-Sanchis, E.; Nadal, Á.; Fernández-Lázaro, F.; Sastre-Santos, Á. *Chem. Commun.* **2011**, 8307–8309; (g) Liu, H.; Wang, Y.; Liu, C.; Li, H.; Gao, B.; Zhang, L.; Bo, F.; Bai, Q.; Ba, X. *J. Mater. Chem.* **2012**, *22*, 6176–6181.
- (a) Diring, S.; Retailleau, P.; Ziessel, R. *J. Org. Chem.* **2007**, *72*, 10181–10193; (b) Gunderson, V. L.; Krieg, E.; Vagnini, M. T.; Iron, M. A.; Rybtchinski, B.; Wasielewski, M. R. *J. Phys. Chem. B.* **2011**, *115*, 7533–7540.
- Queste, M.; Cadiou, C.; Pagoaga, B.; Giraudet, L.; Hoffmann, N. *New J. Chem.* **2010**, *34*, 2537–2545.
- Zhou, Z.; Sarova, G. H.; Zhang, S.; Ou, Z.; Tat, F. T.; Kadish, K. M.; Echegoyen, L.; Guldi, D. M.; Schuster, D. I.; Wilson, S. R. *Chem. Eur. J.* **2006**, *12*, 4241–4248.
- Langhals, H.; Saulich, S. *Chem. Eur. J.* **2002**, *8*, 5630–5643.
- Yang, X.; Xu, X.; Ji, H.-F. *J. Phys. Chem. B.* **2008**, *112*, 7196–7202.
- Würthner, F.; Sautter, A.; Schilling, J. *J. Org. Chem.* **2002**, *67*, 3037–3044.
- Jones, R. A.; Roney, B. D.; Sasse, W. H. F.; Wade, K. O. *J. Chem. Soc. B.* **1967**, 106–111.
- Avlasevich, Y.; Müllen, K. *J. Org. Chem.* **2007**, *72*, 10243–10246.
- Markovic, V.; Villamaina, D.; Barabanov, I.; Daku, L. M. L.; Vauthey, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 7596–7598.
- (a) Ciana, L. D.; Hamachi, I.; Meyer, T. *J. Org. Chem.* **1989**, *54*, 1731–1735; (b) Jang, S.-R.; Lee, C.; Choi, H.; Ko, J. J.; Lee, J.; Vittal, R.; Kim, K.-J. *Chem. Mater.* **2006**, *18*, 5604–5608.
- Würthner, F. *Chem. Commun.* **2004**, 1564–1579.
- Würthner, F.; Stepanenko, V.; Chen, Z.; Saha-Möllner, C. R.; Kocher, N.; Stalke, D. *J. Org. Chem.* **2004**, *69*, 7933–7939.
- Wang, J.; Medlycott, E. A.; Hanan, G. S.; Loiseau, F.; Campagna, S. *Inorg. Chim. Acta* **2007**, *360*, 876–884.