Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 47 (2006) 9083–9087

Tetrahedron Letters

A new tetrathiafulvalene–perylene diimide dyad with a pentaoxa-heptadecane chain as the spacer: metal-ions-induced aggregation

Xiaoping Zheng,[a,b] Deqing Zhang[a,*] and Daoben Zhu[a,*]

[a] *Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100080, China*

Received 15 July 2006; revised 16 October 2006; accepted 17 October 2006
Available online 7 November 2006

Abstract—A new TTF–perylene diimide dyad **1** with a pentaoxa-heptadecane chain as the spacer was synthesized and characterized. Absorption and fluorescent spectral studies of dyad **1** and reference compounds **2** and **3** indicate that aggregation of dyad **1** and compound **2** occurs in the presence of metal ions. Such metal-ions-induced aggregation is likely due to the synergic action of the coordination of metal ions with the oligoethylene glycol unit and the π–π stacking of the perylene diimide unit.

Perylene diimides, initially studied as dyestuffs,[1] have been intensively investigated as electronic materials in recent years due to their optical, redox and stability properties.[2] They are among the best n-type organic semiconductors reported in the literature. High electron mobilities have been described for organic-field-effect transistors with perylene diimides as the semiconductor layers.[3] Perylene diimides are good electron acceptors, and indeed D–A dyads with perylene diimides as the electron acceptor units have been described. We have previously reported tetrathiafulvalene (TTF)–perylene diimide triads and found that the fluorescence is largely quenched due to the photoinduced electron transfer between TTF and perylene diimide units.[4] Recently, Hudlhomme and co-workers have shown that the fluorescence of the tetrathiafulvalene–perylene diimide dyad can be reversibly modulated by the transformation of the TTF unit into its radical cation and dication.[5]

Perylene diimides also show a tendency to aggregate in a solution due to the stacking of the planar π systems.[6] Both absorption and fluorescence spectral changes are observed for perylene diimides upon aggregation.[7] The aggregation of perylene diimides has been achieved through metal ion coordination and H-bonding besides the π–π interaction.[8] Interesting foldmers and nanostructures generated through the assembly of perylene diimides have been reported recently.[9]

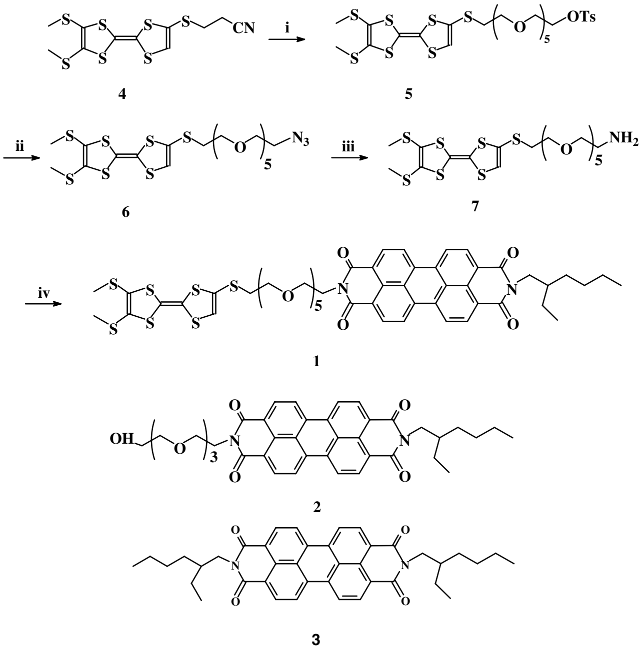
Herein we report a new TTF–perylene diimide dyad **1** (Scheme 1) with a pentaoxa-heptadecane chain as the spacer. According to previous studies,[10] oligoethylene glycol chain is able to coordinate with metal ions, and as a result the separation between the TTF and perylene diimide units would be shortened (Scheme 2). Accordingly, the interaction between TTF and perylene diimide units would be modulated to induce significant fluorescence quenching. However, detailed spectroscopic studies of dyad **1** and the reference compounds **2** and **3** (Scheme 1) indicate that dyad **1** and compound **2** both containing oligoethylene glycol unit, aggregate in the presence of various metal ions.

The synthesis of dyad **1** started from compound **4**,[11] from which compound **5** was prepared after removing 2-cyanoethyl group in the presence of CsOH and sequentially reacting with 1,17-bis-(toluene-4-sulfonyloxy)-3,6,9,12,15-pentaoxa-heptadecane.[12] Compound **5** was transformed to compound **6** after substitution, and the reaction of compound **6** with PPh_3 led to compound **7**. The direct condensation of perylene tetracarboxylic dianhydride with a mixture of 2-ethylhexylamine and compound **7** (1:1 in molar ratio) in DMAc

---

[*] Corresponding authors. E-mail: dqzhang@iccas.ac.cn

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.10.083

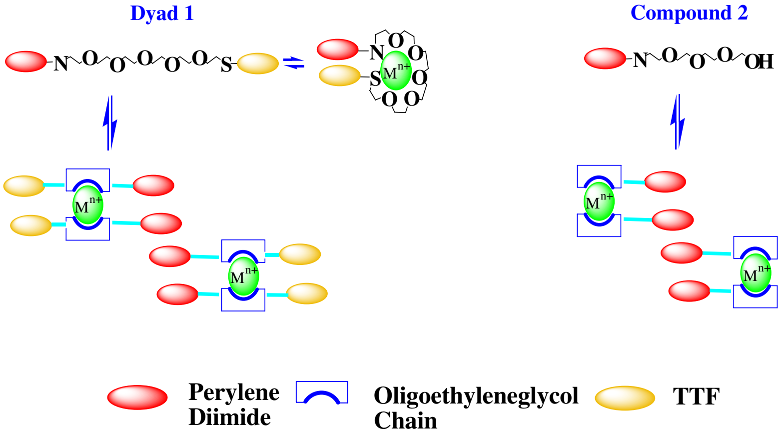


Scheme 1. Reagents: (i) 1,17-bis-(toluene-4-sulfonyloxy)-3,6,9,12,15-pentaoxa-heptadecane, CsOH·H$_2$O; (ii) NaN$_3$, DMF; (iii) PPh$_3$, THF; (iv) perylene-3,4,9,10-tetracarboxylic acid dianhydride, 2-ethylhexylamine, DMAc.

(dimethyl acetamide) led to dyad **1** after careful separation. Similarly, condensation of perylene tetracarboxylic dianhydride with a mixture of 2-ethylhexylamine and 2-{2-[2-(2-amino-ethoxy)-ethoxy]-ethoxy}-ethanol[13] (1:1 in molar ratio) afforded reference compound **2** after separation. Compound **3** was synthesized in an excess of 2-ethylhexylamine.[14]

Compared with compounds **2** and **3**, dyad **1** shows a rather weak fluorescence, a result ascribed to the photo-induced electron transfer (PET) between TTF and perylene diimide units as reported previously.[4,5] When Ca^{2+} was added to the solution of dyad **1**, the fluorescence intensity of dyad **1** decreased gradually and the emission bands at 533 nm and 572 nm were slightly red shifted (Fig. 1A). Simultaneously, the absorption bands of dyad **1** at 524 nm, 488 nm and 458 nm were gradually red shifted and became weak upon addition of Ca^{2+} (Fig. 1B).[15] Such spectral changes for dyad **1** are likely due to the coordination of the oligoethyleneglycol chain with Ca^{2+}. There are two possible ways for the interaction of dyad **1** with Ca^{2+} as shown in Scheme 2: (1) the 'intramolecular coordination of the oligoethyleneglycol chain with Ca^{2+}'; (2) the 'intermolecular coordination of the oligoethyleneglycol chain with Ca^{2+}'. The intramolecular coordination would shorten the separation between the TTF and perylene diimide units, and as a result the interaction between the TTF and perylene diimide units would be increased. On the other hand, the intermolecular coordination would lead to the intermolecular aggregation of dyad **1** in solution. The results from the control experiments with reference compound **2**, as to be discussed below, indicate that the 'intermolecular coordination of the oligoethyleneglycol chain with Ca^{2+}' may be also responsible for the resulting absorption and fluorescent spectral changes of dyad **1** after the addition of Ca^{2+}.

Figure 2 shows the absorption and fluorescent spectra of the reference compound **2** with a tetraethyleneglycol chain unit. The absorption bands at 525 nm, 489 nm and 459 nm were gradually red shifted and their absorption intensities decreased upon the addition of Ca^{2+}.[16] Also, the fluorescence of **2** was gradually reduced in the presence of Ca^{2+}. In comparison, compound **3** without the oligoethyleneglycol chain unit showed no variation in both absorption and fluorescence spectra in the presence of Ca^{2+} under the same condition. Thus, the spectral variation of **2** should be a reflection of the interaction of the oligoethyleneglycol unit with Ca^{2+}. As there is no TTF unit in compound **2**, such spectral changes cannot be ascribed to the 'intramolecular coordination of the oligoethyleneglycol chain with Ca^{2+}'. Moreover, the spectral changes of **2** in the presence of Ca^{2+} are rather similar to those of perylene diimides upon aggregation reported previously.[7] Therefore, it may be concluded that the aggregation of **2** occurred in the presence of Ca^{2+} through the synergic effect of the coordination of Ca^{2+} with oligoethylene glycol chain and π–π stacking of the perylene diimide unit (Scheme 2). The intermolecular coordination mode of Ca^{2+} with the oligoethyleneglycol chain is not clear at this stage



Scheme 2. The possible coordination modes of metal ions with the oligoethylene glycol chain and resulting aggregation of dyad **1** and compound **2**.

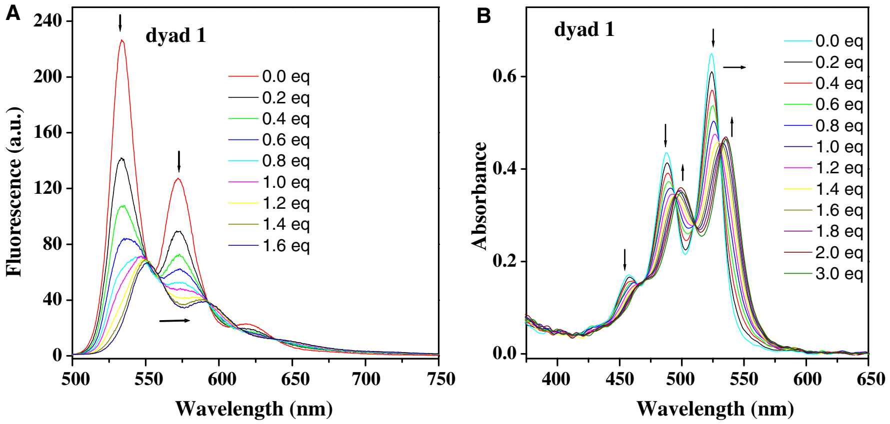


Figure 1. Fluorescence (A) and absorption spectra (B) of dyad **1** (1.0×10^{-5} M in CH_2Cl_2) after the addition different amounts of $Ca(ClO_4)_2$ (dissolved in CH_3CN); arrows indicate the direction of spectral change by increasing the amounts of $Ca(ClO_4)_2$.

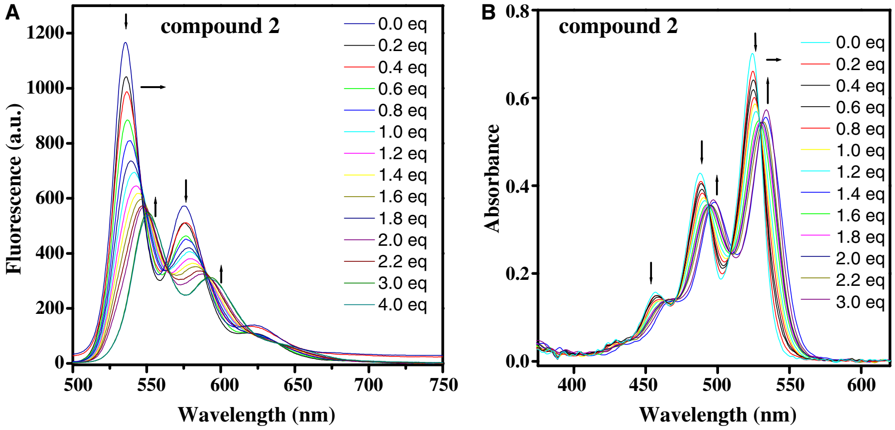


Figure 2. Fluorescence (A) and absorption spectra (B) of compound **2** (1.0×10^{-5} M in CH_2Cl_2) after the addition different amounts of $Ca(ClO_4)_2$ (dissolved in CH_3CN); arrows indicate the direction of spectral change by increasing the amounts of $Ca(ClO_4)_2$.

although two possible coordination modes are proposed in Scheme 2.

It is obvious that similar absorption and fluorescent spectral changes occurred to dyad **1** and reference compound **2** upon the addition of Ca^{2+}. Therefore, it is reasonably assumed that the 'intermolecular coordination of the oligoethyleneglycol chain with Ca^{2+}' the resulting aggregation (Scheme 2) also contribute to the spectral changes of dyad **1** in the presence of Ca^{2+}. According to previous studies,[6–9] stacking of perylene diimide units results in absorption spectral changes and the pending TTF units, would further quench the fluorescence of the perylene diimide unit through PET process.[17]

The ^1H NMR spectral measurements made for dyad **1** and compound **2** also provided evidence for their aggregation in the presence of Ca^{2+}. After addition of 1.0 equiv of Ca^{2+} to the $CDCl_3$ solution (ca. 1 mM) of dyad **1**, the chemical shifts for the protons of $–CH_2$ unit of the spacer were down-field shifted by ca. 0.10 ppm while those of the perylene diimide unit were up-field shifted by ca. 0.11 ppm. Similar result was observed for compound **2**. It is understandable that coordination of the oligoethylene glycol unit with Ca^{2+} would induce down-field shifts for the protons of the $–CH_2$ unit of the spacer. According to previous results,[9b,18] aggregation of the perylene diimide unit results in up-field shifts for the perylene aromatic protons.

In addition, the perylene–spacer–perylene diimide in which the spacer contained the oligoethyleneglycol units was synthesized (see page S4–S5 Supplementary data). The absorption bands became gradually weak and red shifted upon the addition of Ca^{2+}. Also, the intensities of the fluorescent bands were reduced gradually in the presence of Ca^{2+} (see Fig. S11 of Supplementary data). These results indicated that aggregation occurred for the perylene–spacer–perylene diimide in the presence of Ca^{2+}.

Besides Ca^{2+}, other metal ions (Li^+, Na^+, K^+, Ba^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Gd^{3+}) were also tested. For instance, Figure 3 shows the absorption spectral changes of dyad **1** and compound **2** upon the addition of Gd^{3+}; the intensities of absorption bands at 525 nm, 489 nm and 459 nm decreased gradually with obvious red-shifts. These results imply that Gd^{3+} can also induce the aggregation of dyad **1** and compound **2**. Minor absorption spectral variation was also detected for dyad **1** and

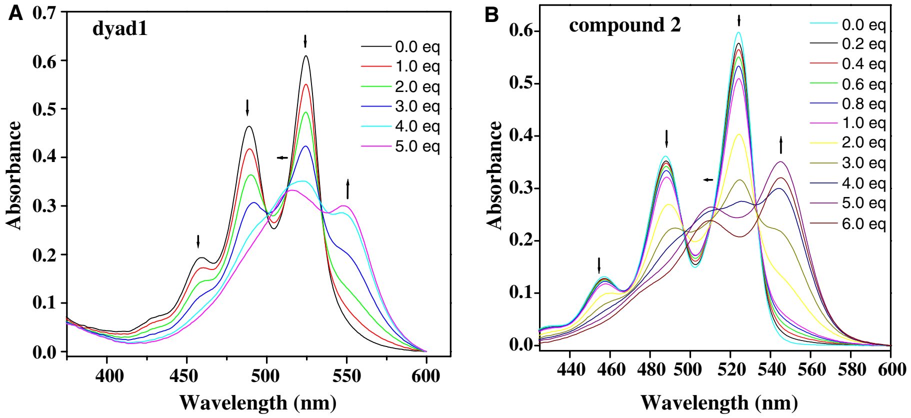


Figure 3. Absorption spectra of dyad **1** (A) (1.0×10^{-5} M in CH_2Cl_2) and compound **2** (B) (1.0×10^{-5} M in CH_2Cl_2) after the addition of different amounts of $Gd(ClO_4)_3$ dissolved in acetonitrile; arrows indicate the direction of spectral change by increasing the amounts of $Gd(ClO_4)_3$.

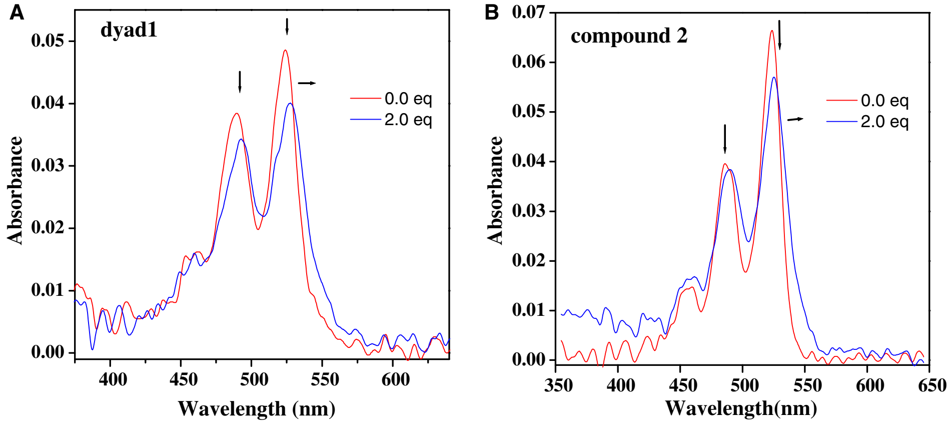


Figure 4. Absorption spectra of dyad **1** (1.0×10^{-6} M in CH_2Cl_2) (A) and compound **2** (B) (1.0×10^{-6} M in CH_2Cl_2) after the addition of different amounts of Ca^{2+} dissolved in acetonitrile; arrows indicate the direction of spectral change by increasing the amounts of Ca^{2+}.

compound **2** upon addition of Li^+ (see Figs. S1 and S6 of Supplementary data), but there was no absorption spectral change in the presence of Na^+ and K^+ (even 5.0 equiv of amounts of Na^+/K^+ were present). The different effects of metal ions on the absorption spectra of dyad **1** and compound **2** may be related to their different binding abilities with the oligoethyleneglycol chain.

The absorption spectra of dyad **1** and compound **2** could not be measured at a high concentration due to their low solubilities in organic solvents. On the other hand, the absorption spectra of dyad **1** and compound **2** were recorded at a low concentration in the absence and presence of metal ions. As shown in Figure 4, even when the concentration of dyad **1** and compound **2** was reduced to 1.0×10^{-6} M, their absorption spectra became weak and red shifted upon the addition of Ca^{2+}, implying the aggregation of dyad **1** and compound **2** occurred even at such a low concentration.

In summary, a new TTF–perylene diimide dyad **1** with a pentaoxa-heptadecane chain as the spacer was synthesized and characterized. Absorption and fluorescent spectral studies of dyad **1** and reference compounds **2** and **3** indicate that the aggregation of dyad **1** and compound **2** occurs in the presence of metal ions. Such metal-ions-induced aggregation is likely due to the synergic action of the coordination of metal ions with the oligoethyleneglycol unit and the π–π stacking of the perylene diimide units (Scheme 2). It should be noted that the aggregation of perylene diimides under the influences of metal ions were scarcely described. Further studies of the perylene diimides with different oligoethylene glycol units are under way.

Acknowledgments

The present research was financially supported by NSFC and Chinese Academy of Sciences. D.-Q.Z. thanks the National Science Fund for Distinguished Young Scholars.

Supplementary data

Experimental details for the synthesis of dyad **1**, compound **2** and the perylene diimide–spacer–perylene diimide; absorption and fluorescence spectra of dyad **1** and compound **2** in the presence of metal ions; absorption and fluorescence spectra of the perylene diimide–spacer–perylene diimide in the presence of Ca^{2+}. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.083.

References and notes

1. (a) Zollinger, H. *Color Chemistry, Synthesis, Properties, and Applications of Organic Dyes and Pigments*, 3rd ed.; Wiley-VCH: Weinheim, 2003; (b) Herbst, W.; Hunger, K. *Industrial Organic Pigments: Production, Properties, Applications*, 2nd ed.; Wiley-VCH: Weinheim, 1997.
2. (a) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449–486; (b) Schmidt-Mende, L.; Fechtenhotter, A.; Müllen, K.; Moons, E.; Friend, R. H.; Mackenzie, J. D. *Science* **2001**, *293*, 1119–1122; (c) Yskimov, A.; Forrest, S. R. *Appl. Phys. Lett.* **2002**, *80*, 1667–1669; (d) Ren, J.; Wang, Q.; Qu, D.; Zhao, X.; Tian, H. *Chem. Lett.* **2004**, *33*, 974–975; (e) Ren, J.; Zhao, X.; Wang, Q.; Ku, C.; Qu, D.; Chang, C.; Tian, H. *Dyes Pigments* **2005**, *64*, 193–200.
3. (a) Struijk, C. W.; Sieval, A. B.; Dakhorst, J. E. J.; van Dijk, M.; Kimkes, P.; Koehorst, R. B. M.; Donker, H.; Schaafsma, T. J.; Picken, S. J.; van de Craats, A. M.; Warman, J. M.; Zuihof, H.; Sudholter, E. J. R. *J. Am. Chem. Soc.* **2000**, *122*, 11057–11066; (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99–117; (c) Lee, S. K.; Zu, Y. B.; Herrmann, A.; Geerts, Y.; Müllen, K.; Bard, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 3513–3520; (d) Quante, H.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1323–1325; (e) Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037–1039.
4. Guo, X.; Zhang, D.; Zhang, H.; Fan, Q.; Xu, W.; Ai, X.; Fan, L.; Zhu, D. *Tetrahedron* **2003**, *59*, 4843–4850.
5. Leroy-Lhez, S.; Baffreau, J.; Perrin, L.; Levillain, E.; Allain, M.; Blesa, M.-J.; Hudlhomme, P. *J. Org. Chem.* **2005**, *70*, 6313–6320.
6. Balakrishnam, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 7390–7398.
7. Würthner, F. *Chem. Commun.* **2004**, 1564–1579, and references therein.
8. Würthner, F.; Thalacker, C.; Sautter, A.; Schartl, W.; Ibach, W.; Hollricher, O. *Chem. Eur. J.* **2000**, *6*, 3871–3886.
9. (a) Wang, W.; Han, J. J.; Wang, L.-Q.; Li, L.-S.; Shaw, W. J.; Li, A. D. Q. *Nano Lett.* **2003**, *3*, 455–458; (b) Wang, W.; Li, L.-S.; Helms, G.; Zhou, H.-H.; Li, A. D. Q. *J. Am. Chem. Soc.* **2003**, *125*, 1120–1121; (c) Yan, P.; Chowdhury, A.; Holman, M. W.; Adams, D. M. *J. Phys. Chem. B* **2005**, *109*, 724–730; (d) Gesquiere, A. J.; Uwada, T.; Asahi, T.; Masuhara, H.; Barbara, P. F. *Nano Lett.* **2005**, *5*, 1321–1325.
10. Baran, P. S.; Monaco, R. R.; Khan, A. U.; Schuster, D. I.; Wilson, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 8363–8364.
11. (a) Jia, C.; Zhang, D.; Xu, W.; Zhu, D. *Org. Lett.* **2001**, *3*, 1941–1944; (b) Jia, C.; Zhang, D.; Guo, X.; Wan, S.; Xu, W.; Zhu, D. *Synthesis* **2002**, *15*, 217.
12. Ouchi, M.; Inoue, Y.; Liu, Y.; Nagamune, S.; Nakamura, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1260–1262.
13. Svedhem, S.; Hollander, C.-A.; Shi, J.; Konradsson, P.; Liedberg, B.; Svensson, S. C. T. *J. Org. Chem.* **2001**, *66*, 4494–4503.
14. Adachi, M.; Murata, Y.; Nakamura, S. *J. Phys. Chem.* **1995**, *99*, 14240–14246.
15. Based on the plot of $1/(A - A_o)$ versus the reciprocal of $[Ca^{2+}]$, where A and A_o refer to the absorbance at 540 nm in the presence and absence of Ca^{2+}, respectively, the binding constant of dyad **1** with Ca^{2+} was estimated to be 9.5×10^3. The free binding energy was calculated to be $-22.69\ \mathrm{kJ\ mol^{-1}}$.
16. The binding constants of compound **2** with Ca^{2+} was estimated to be 1.02×10^4. The free binding energy was calculated to be $-22.87\ \mathrm{kJ\ mol^{-1}}$.
17. Since the absorption bands are bathochromically shifted, *J*-aggregates are assumed to be formed for dyad **1** in the presence of Ca^{2+}.
18. Rybtchinski, B.; Sinks, L. E.; Wasielewaski, M. R. *J. Phys. Chem. A* **2004**, *108*, 7497–7505.