International Edition: DOI: 10.1002/anie.201505185
German Edition: DOI: 10.1002/ange.201505185

Precise Design of Phosphorescent Molecular Butterflies with Tunable Photoinduced Structural Change and Dual Emission

Chenkun Zhou, Yu Tian, Zhao Yuan, Mingu Han, Jamie Wang, Lei Zhu, Maliheh Shaban Tameh, Chen Huang, and Biwu Ma**

Abstract: *Photoinduced structural change (PSC) is a fundamental excited-state dynamic process in chemical and biological systems. However, precise control of PSC processes is very challenging, owing to the lack of guidelines for designing excited-state potential energy surfaces (PESs). A series of rationally designed butterfly-like phosphorescent binuclear platinum complexes that undergo controlled PSC by Pt–Pt distance shortening and exhibit tunable dual (greenish-blue and red) emission are herein reported. Based on the Bell–Evans–Polanyi principle, it is demonstrated how the energy barrier of the PSC, which can be described as a chemical-reaction-like process between the two energy minima on the first triplet excited-state PES, can be controlled by synthetic means. These results reveal a simple method to engineer the dual emission of molecular systems by manipulating PES to control PSC.*

Molecular excited states obtained by photoexcitation are the foundation for solar energy conversion, photocatalysis, and molecular machines.[1] Detailed studies of the excited-state properties of molecules, including their structures, energetics, and decay pathways, provide a better understanding of photoinduced chemical and biological processes, and enable the development of new functional materials and devices. Among major excited-state dynamic processes of molecular systems, photoinduced structural change (PSC) has recently become a very active research field owing to the advent of ultrafast time-resolved spectroscopic methods and X-ray spectroscopy.[2] Copper(I) complexes with phenanthroline derivatives, which exhibit photoinduced "flattening" in the metal-to-ligand charge transfer (MLCT) excited state, have been thoroughly studied by several groups.[2a–j] The real-time observation of the excited-state dynamics and complementary quantum-chemical calculations have provided a clear picture of the electronic relaxation and ultrafast structural distortion of these compounds. Another well-known PSC is the ultrafast contraction of the Pt–Pt distance in binuclear platinum(II) complexes.[2k–r] Experimental studies of PSC processes in several platinum complexes, such as $[Pt_2(pop)_4]^{4-}$ (pop $= P_2O_5H_2^{2-}$) and $[Pt(ppy)(\mu\text{-}t\mathrm{Bu}_2pz)_2]$ (ppy = 2-phenylpyridyl, $t\mathrm{Bu}_2$pz = 3,5-di-*tert*-butylpyrazolyl), have provided direct evidence for a Pt–Pt contraction of 0.2–0.4 Å in the excited state, which is consistent with theoretical calculations.[2o–r] PSC processes have also been observed in purely organic molecular systems, such as azobenzenes and stilbenes.[1c–e] Despite significant advances in our understanding of the PSC processes in these molecular systems, to the best of our knowledge, the precise control of PSC processes has not been demonstrated for any molecular system thus far.

Recently, we reported a butterfly-like pyrazolate-bridged binuclear platinum complex, BFPtPZ, which undergoes PSC by shortening of the Pt–Pt distance.[3] Unlike the ultrafast photoinduced flattening of Cu^I complexes and the Pt–Pt contraction in typical platinum complexes that leads to one excited-state energy minimum and single emission, BFPtPZ undergoes PSC between two excited structures on the first triplet excited-state potential energy surface (PES), which results in dual emission, that is, greenish-blue emission from the excited state with the long Pt–Pt distance and red emission from the excited state with the short Pt–Pt distance. The effect of the molecular structure on PSC has been studied for a few pyrazolate-bridged dinuclear platinum complexes. Among these complexes, BFPtPZ is the only one with dual emission; molecules based on other cyclometallating ligands, such as 2-(2′-thienyl)pyridine or 2-phenylpyridine, do not exhibit PSC or dual emission.[2q,r,3,4] By introducing bulky groups to the 3- and 5-positions of the pyrazolate bridges, the emission can be shifted to significantly lower energies.[2q,r,3,4] Substituent effects on PSC have also been observed for Cu^I complexes: Derivatives with bulkier substituents at the 2- and 9-positions of the phenanthroline ligand require longer periods of time for flattening, 200 fs for $[Cu(phen)_2]^+$ (phen = 1,10-phenanthroline), 660 fs for $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline), and 920 fs for $[Cu(dpphen)_2]^+$ (dpphen = 2,9-diphenyl-1,10-phenanthroline).[2c,d] All of these findings suggest that PSC processes could be manipulated by precise control of the molecular structure.

Herein, we report a series of rationally designed butterfly-like phosphorescent binuclear platinum complexes that

---

[*] C. Zhou, Dr. Z. Yuan, Dr. M. Han, Prof. B. Ma
Chemical and Biomedical Engineering
FAMU-FSU College of Engineering (USA)
E-mail: bma@fsu.edu

Y. Tian, Prof. C. Huang, Prof. B. Ma
Materials Science Program, Florida State University (USA)
E-mail: chuang3@fsu.edu

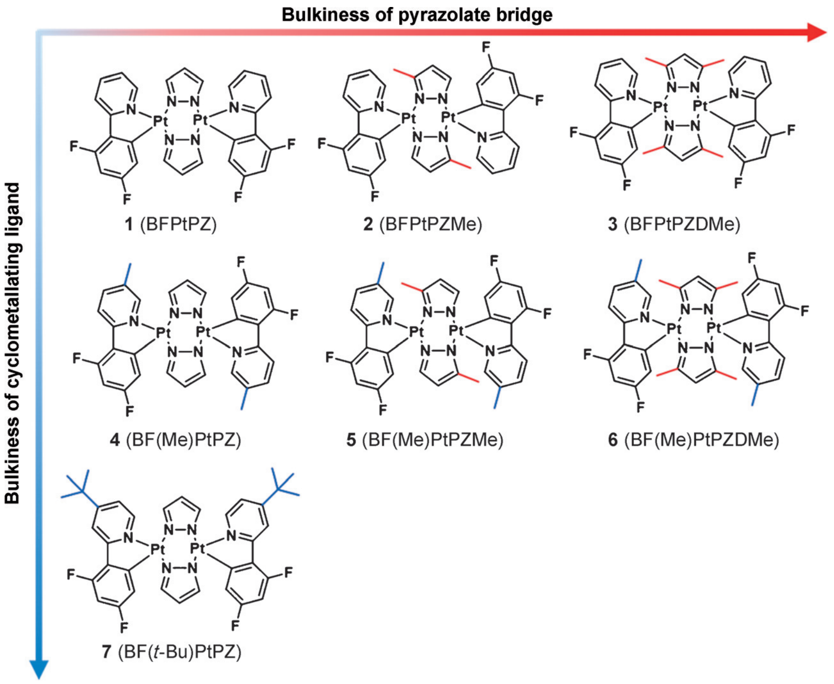
Dr. Z. Yuan, J. Wang, Prof. L. Zhu, Prof. B. Ma
Department of Chemistry and Biochemistry
Florida State University (USA)

M. S. Tameh, Prof. C. Huang
Department of Scientific Computing
Florida State University (USA)

Supporting information for this article, including details on the synthesis and characterization as well as DFT calculations of the complexes studied herein, is available on the WWW under http://dx.doi.org/10.1002/anie.201505185.

undergo controlled PSC by Pt–Pt distance shortening and exhibit tunable dual emission of greenish-blue and red light in the steady state. The unique butterfly-like structure of these complexes offers two handles for changing the molecular structure: the cyclometallating ligand (the butterfly wings) and the pyrazolate bridge (the butterfly body). We demonstrate that the energy barrier separating the two lowest energy states on the first triplet excited-state PES can be precisely tuned by simply adjusting the relative energy between these two states, based on the Bell–Evans–Polanyi principle.[5] Such a simple scheme serves to achieve very precise control over the PSC and dual-emission processes.

The chemical structures of seven pyrazolate-bridged platinum binuclear complexes (major isomers), which can also be considered as molecular butterflies, are shown in Scheme 1. The syntheses of these molecules followed the three major steps previously reported for the preparation of BFPtPZ (**1**).[6] The cyclometallating ligands were prepared by Suzuki couplings.[7] Reacting the cyclometallating ligand with potassium tetrachloroplatinate afforded the chloride monomers, which reacted with the pyrazolate bridging ligands in the presence of a base to yield pyrazolate-bridged binuclear platinum complexes. The products were purified by column chromatography and recrystallization. ^{1}H NMR spectroscopy and MALDI spectrometry were used to characterize the synthesized products. Most of these molecules were isolated as a mixture of the *cis* and *trans* isomers with respect to the relative orientation of the two cyclometallating ligands, except for molecule **7**, which was only present as its *cis* isomer, as suggested by ^{1}H NMR spectroscopy.[4b,6] We performed unrestricted Kohn–Sham density functional theory (DFT) calculations to study the ground-state and first triplet excited-state PESs of these molecules.[8] Our approach is similar to that of Sakaki et al. on molecules **1** and **3**.[9] The product compositions for each molecule can be explained by comparing the DFT ground-state energies of the different isomers. A small energy difference of approximately 0.006 eV was observed for the isomers of molecules **1**–**6**, which is consistent with the formation of products **1**–**6** as mixtures of isomers. On the other hand, a relatively large energy difference was calculated for the isomers of **7**, that is, the *cis* form is 0.189 eV lower in energy than the *trans* form, which is consistent with the sole formation of the *cis* isomer.



Scheme 1. Chemical structures of pyrazolate-bridged binuclear platinum complexes with difluorophenylpyridine (dfppy) based ligands as the butterfly wings and pyrazolate (PZ) ligands as the butterfly body.

All seven molecules are light-yellow solids. Their absorption spectra in dichloromethane (DCM) solution at room temperature are of similar shapes and intensities (Figure 1 a). The lowest structured absorption at around 465 nm can be assigned to the spin-forbidden mixed ligand center/metal-to-ligand charge transfer (^{3}LC/MLCT) transition, suggesting little to no Pt–Pt metal-metal-to-ligand charge transfer (MMLCT). In other words, all of these molecular

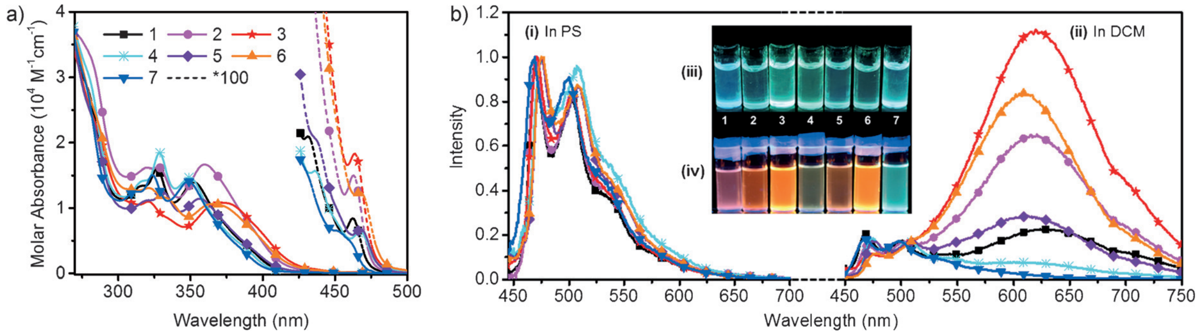


Figure 1. a) Absorption spectra of molecules **1**–**7** in DCM solution at room temperature, the dashed lines represent a 100-fold magnification of the solid lines. b) i, ii) Normalized emission spectra of molecules **1**–**7** in the solid state (in PS, i) and in DCM solution (ii) at room temperature. iii, iv) Photographs of molecules **1**–**7** in PS (iii) and in DCM solution (iv) under UV light.

butterflies keep their wings spread in their ground states and right after photoexcitation. This is consistent with the lowest energy states on the calculated ground-state PESs featuring long Pt–Pt distances (Supporting Information, Figure S4). The emission spectra of all seven molecules in polystyrene (PS) and in DCM solution ($\lambda_{ex} = 360$ nm) are shown in Figure 1 b (i and ii); the corresponding photographs under UV excitation are also shown (iii and iv). All seven molecules show very similar greenish-blue emission in PS, as the structures of the molecules and their dynamics in the excited states are greatly constrained. Dual emission was clearly observed for all molecules, apart from complex **7**, in solution, as the molecules can easily change their structures and their excited-state dynamics are no longer constrained. It is noteworthy that the emission behavior of all molecules is the same at any excitation wavelength and independent of the solution concentration. The photoluminescence quantum yields of the seven molecules in DCM at room temperature were measured to be 1.92 (**1**), 2.75 (**2**), 2.84 (**3**), 1.32 (**4**), 1.36 (**5**), 2.18 (**6**), and 0.71 % (**7**). By splitting the dual emission into greenish-blue and red emission (Figure S1), we obtained quantum yields of 0.41 and 1.51 (**1**), 0.19 and 2.56 (**2**), 0.10 and 2.74 (**3**), 0.74 and 0.58 (**4**), 0.28 and 1.08 (**5**), 0.12 and 2.06 (**6**), and 0.71 and 0 % (**7**) for greenish-blue and red emission, respectively (Table S1). When the bulkiness of the cyclometallating ligand was increased through attaching methyl and *tert*-butyl groups to the 2-(2,4-difluorophenyl)pyridine (dfppy) ligand, the red/blue emission ratio decreased. To produce dual emission with higher red/blue ratios, we increased the bulkiness of the pyrazolate bridge by replacing simple pyrazole (PZ) with 3-methylpyrazole (PZMe) and 3,5-dimethylpyrazole (PZDMe). It should be pointed out that the introduction of methyl or bulky *tert*-butyl groups does not significantly affect the polarity, the dipole moment, or the electronic structure of the cyclometallating and bridging ligands. The only parameter being changed is the steric bulk, which affects the molecular space filling (Figure S5). Overall, among the library of molecular butterflies with different bodies (pyrazolate bridges) and wings (cyclometallating ligands), molecule **3**, with the bulkiest body (PZDMe) and lightest wings (dfppy), emitted mostly red light; molecule **7**, with the lightest body (PZ) and bulkiest wings (*t*Bu-dfppy), emitted only greenish-blue light. Other molecules, which are based on different combinations of bodies and wings, display dual emission with different red/blue ratios. By means of molecular engineering, we can thus precisely control the luminescence properties of a family of molecular butterflies.

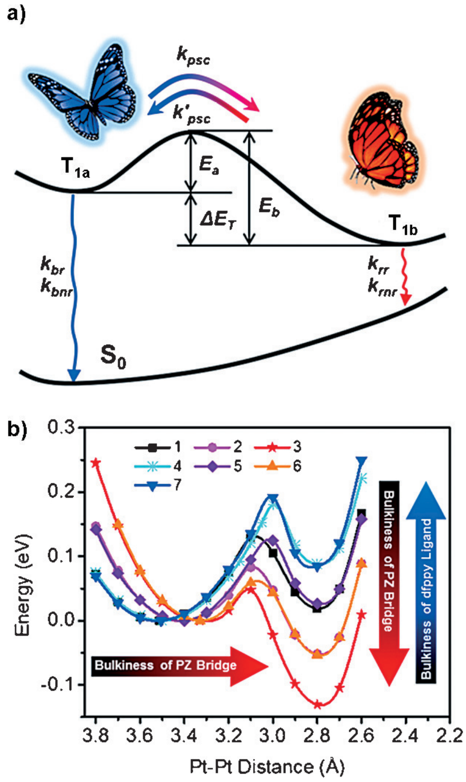


Figure 2. Excited-state dynamics and potential energy surfaces of the molecular butterflies. a) Schematic representation of the PSC processes, transitions between various electronic states, and dual emission. E_a and E_b are the energy barriers, ΔE_T is the energy difference between the T_{1a} and T_{1b} states, k_{PSC} is the rate of PSC from T_{1a} to T_{1b}, k'_{PSC} is the rate of reverse PSC, k_{br} and k_{rr} are the radiative decay rates of the greenish-blue and red emissions, and k_{bnr} (without accounting for k_{PSC}) and k_{rnr} (without accounting for k'_{PSC}) are the non-radiative decay rates for T_{1a} and T_{1b}. b) Calculated potential energy surfaces of the first triplet excited state versus the Pt–Pt distance for the molecular butterflies **1**–**7**.

The dual emission of BFPtPZ (**1**) is due to the competition between the two local minima on the first triplet excited-state PES: a greenish-blue emission from the T_{1a} excited state with ^{3}LC/MLCT characteristics at a long Pt–Pt distance, and a red emission from the T_{1b} excited state with ^{3}MMLCT characteristics at a short Pt–Pt distance (Figure 2 a).[3] The PSC can therefore be considered as a chemical-reaction-like process taking place on the first triplet excited-state PES, with T_{1a} as the reactant and T_{1b} as the product. Considering the fact that the greenish-blue emission and the red emission have almost identical decay behaviors,[3] the PSC of BFPtPZ (**1**) is believed to take place very rapidly after intersystem crossing, and the T_{1a} and T_{1b} states reach equilibrium while they emit phosphorescence. Combining our DFT results, we attempted to gain a more fundamental understanding of the excited-state dynamics of these molecular butterflies. Precise control over the dual emission of these molecular butterflies is realized in two steps: 1) The PSC kinetics and excited-state equilibria are controlled by precisely engineering the positions of the T_{1a} and T_{1b} states and the energy barriers separating them on the first triplet excited-state PES; 2) a theoretical connection between the energy barrier and the dual-emission characteristics is made.

To precisely control the PSC processes and the dual emission, a fine-tuning of the energy barrier E_a is required. The T_{1a} states of all molecules were shifted to the same energy (Figure 2 b). As a good approximation, the first triplet excited-state PES of these molecules can be considered as the superposition of the two parabolic PESs of T_{1a} and T_{1b} if the position of the transition state as a function of the reaction coordinate remains the same in this series of molecules. Therefore, a nearly linear correlation between the energy barrier E_a and the energy difference ΔE_T between T_{1a} and T_{1b}

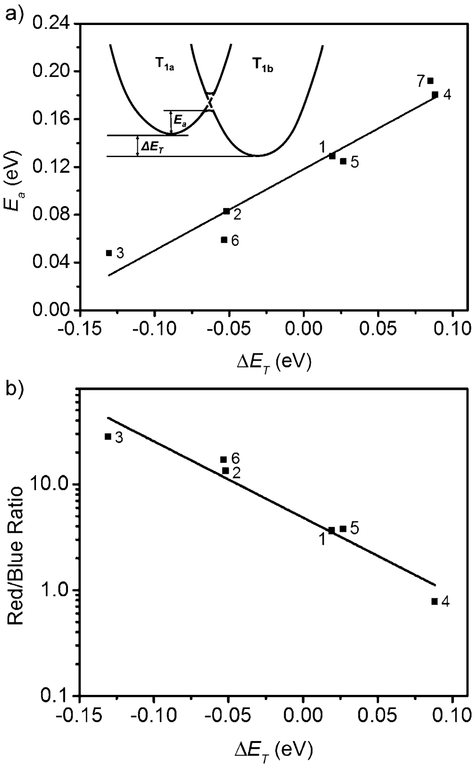


Figure 3. Theoretical modeling of the tuning of the energy barrier and its correlation with the experimentally determined PSC rate. a) Bell–Evans–Polanyi plots of the energy barrier (E_a) versus the energy difference between T_{1a} and T_{1b} (ΔE_T). The inset illustrates the Bell–Evans–Polanyi principle. b) Dependence of the experimentally determined red/blue luminescence intensity ratios in solution on the energy difference between T_{1a} and T_{1b} (ΔE_T).

states is expected (Figure 3a) because of the Bell–Evans–Polanyi principle.[5] Consequently, a desired energy barrier E_a can simply be obtained by adjusting the relative energies of T_{1a} and T_{1b} by molecular engineering. DFT calculations show that the steric bulk of the pyrazolate bridging ligands influences both the T_{1a} and T_{1b} states. As the steric bulk of the bridging ligands increases, the T_{1a} state (^{3}LC/MLCT) shifts to slightly shorter Pt–Pt distances and the T_{1b} state (^{3}MMLCT) is stabilized to lower energies with slightly more localized Pt–Pt molecular orbitals. This is due to the fact that the bulky groups attached to the bridging ligands can force the two butterfly wings closer together in the T_{1a} state and confine the Pt–Pt molecular orbitals in the T_{1b} state by space filling. On the other hand, the steric bulk of the cyclometallating ligand has little to no impact on the T_{1a} state, because the cyclometallating ligands are far away from each other with almost no interaction between the attached methyl or bulky *tert*-butyl groups when the butterfly wings are open. However, when the butterfly wings get closer to each other at shorter Pt–Pt distances, bulkier cyclometallating ligands will destabilize the T_{1b} state to higher energies with slightly stretched Pt–Pt molecular orbitals. Overall, the steric bulk affects the molecular space filling and the energy of the molecular orbitals, especially the Pt–Pt d_{z^2} anti-bonding orbitals in the T_{1b} state (Figure S5). Interestingly, with methyl substituents, the degree by which T_{1b} is lowered because of the bulky bridging ligand is similar to the degree by which T_{1b} increases in energy because of the bulky cyclometallating ligand. Overall, the energy barriers and T_{1b} increase in the order of **3** < **6** < **2** < **5** < **1** < **4** < **7**. These DFT results are in line with our experimental findings: The red/blue ratios of the dual emissions for molecules **1**–**7** decrease in the order of **3** > **6** > **2** > **5** > **1** > **4** > **7**. The bulky groups have the same effects on the ground state (S_0), that is, a bulkier pyrazolate bridge shifts the lowest S_0 state to a shorter Pt–Pt distance (corresponding to T_{1a}) and stabilizes S_0 at a short Pt–Pt distance (corresponding to T_{1b}); bulkier cyclometallating ligands have little to no impact on the S_0 state at long Pt–Pt distances (corresponding to T_{1a}), but destabilize S_0 at short Pt–Pt distances (corresponding to T_{1b}). As different bulky groups shift the singlet ground-state and triplet excited-state PESs by approximately the same small amount of energy, we observed similar peak positions for the dual emissions of the different molecules. It is important to keep in mind that the intensity ratio between the red and greenish-blue emissions is determined by PSC.

To quantitatively describe how the potential energy surface and PSC control the dual-emission spectra in solution, we established the correlations between several emission characteristics, namely the red/blue ratios, PSC rates, and energy barriers. As the excited states can rapidly reach equilibrium at T_{1a} and T_{1b} after photoexcitation when the energy barriers are small (Figure 2a), the ratio of the populations of T_{1b} and T_{1a} is equal to $k_{\mathrm{PSC}}/k'_{\mathrm{PSC}}$. The red/greenish-blue emission intensity ratio (red/blue) is equal to $[(k_{\mathrm{PSC}}k_{\mathrm{rr}})/(k_{\mathrm{rr}}+k_{\mathrm{rnr}})]/[(k'_{\mathrm{PSC}}k_{\mathrm{br}})/(k_{\mathrm{br}}+k_{\mathrm{bnr}})]$, where k_{rr} and k_{br} are the radiative decay rates of the red and greenish-blue emissions, and k_{rnr} and k_{bnr} are the non-radiative decay rates (without accounting for PSC) of the T_{1a} and T_{1b} states. As the greenish-blue and red emissions have almost identical decay curves (Figure S2), the red/blue ratio of the dual emission can be considered to be proportional to the ratio of the PSC rates, $k_{\mathrm{PSC}}/k'_{\mathrm{PSC}}$ (see the Supporting Information). The correlations between the PSC rates and the energy barriers can be described by the Arrhenius equation,[10] $k_{\mathrm{PSC}} = Ae^{-E_a/(RT)}$ and $k'_{\mathrm{PSC}} = Ae^{-E_b/(RT)}$, where A is the pre-exponential factor, E_a is the energy barrier going from T_{1a} to T_{1b}, E_b is the energy barrier going from T_{1b} to T_{1a}, and R is the universal gas constant. Based on this analysis, we expect an exponential correlation between the red/blue ratios and the energy difference (ΔE_T) between T_{1a} and T_{1b}. An Arrhenius plot is given in Figure 3b, which clearly validates our simple scheme for the design of the excited-state PES to control the PSC and excited-state equilibrium, which consequently determine the dual emission. This dependence of the emission spectra on the molecular structures clarifies why simple pyrazole-bridged binuclear platinum complexes with other ligands, such as 2-(2′-thienyl)pyridine or 2-phenylpyridine, do not show dual emission.[2q,r,3,4] These complexes, based on cyclometallating ligands with a lower energy than dfppy, have a lower T_{1a}, but a similar T_{1b} state, resulting in a larger energy barrier E_a, which prevents PSC from T_{1a} to T_{1b}.

In summary, we have demonstrated how molecular engineering can be employed to achieve precise and widerange control over the dual emission of a library of phosphorescent molecular butterflies based on pyrazolate-bridged binuclear platinum complexes. Our approach relies on the fine-tuning of the energy barrier for the photoinduced structural change on the excited-state potential energy surface, based on the Bell–Evans–Polanyi principle. A quantitative description of the precise manipulation of the energy barrier for the control of the photoinduced structural change and the dual emission has been established by treating photoinduced structural change as a chemical reaction on the excited-state potential energy surface from the initial wing-spread state to the final wing-folded state. Complementary experimental and computational efforts significantly advanced our fundamental understanding of these processes. It was highlighted how the excited-state dynamics of photoactive molecular systems could eventually be controlled, and the feasibility of using computational predictions to guide the development of materials with desired properties in a rational manner was demonstrated. Detailed studies of the excited-state kinetics of these molecular butterflies using ultrafast spectroscopic methods and investigations on their applications as molecular sensors and machines are underway.

Acknowledgements

We acknowledge the Florida State University for financial support through the Energy and Materials Initiative. L.Z. acknowledges the National Science Foundation (CHE1213574). We thank Dr. Kenneth Hanson for helpful discussions.

Keywords: dual emission · excited states · molecular dynamics · photochemistry · platinum complexes

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9591 – 9595
Angew. Chem. **2015**, *127*, 9727 – 9731

[1] a) C. W. Tang, *Appl. Phys. Lett.* **1986**, *48*, 183 – 185; b) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737 – 740; c) A. Credi, *Aust. J. Chem.* **2006**, *59*, 157 – 169; d) V. Balzani, A. Credi, M. Venturi, *Chem. Soc. Rev.* **2009**, *38*, 1542 – 1550; e) M. von Delius, D. A. Leigh, *Chem. Soc. Rev.* **2011**, *40*, 3656 – 3676; f) A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022 – 4047; g) A. W. Hains, Z. Q. Liang, M. A. Woodhouse, B. A. Gregg, *Chem. Rev.* **2010**, *110*, 6689 – 6735; h) J. Z. Zhao, W. H. Wu, J. F. Sun, S. Guo, *Chem. Soc. Rev.* **2013**, *42*, 5323 – 5351; i) X. D. Wang, O. S. Wolfbeis, R. J. Meier, *Chem. Soc. Rev.* **2013**, *42*, 7834 – 7869; j) M. A. Henderson, I. Lyubinetsky, *Chem. Rev.* **2013**, *113*, 4428 – 4455.

[2] a) M. Iwamura, S. Takeuchi, T. Tahara, *J. Am. Chem. Soc.* **2007**, *129*, 5248 – 5256; b) M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi, T. Tahara, *J. Am. Chem. Soc.* **2011**, *133*, 7728 – 7736; c) M. Iwamura, S. Takeuchi, T. Tahara, *Phys. Chem. Chem. Phys.* **2014**, *16*, 4143 – 4154; d) J. V. Lockard, S. Kabehie, J. I. Zink, G. Smolentsev, A. Soldatov, L. X. Chen, *J. Phys. Chem. B* **2010**, *114*, 14521 – 14527; e) L. X. Chen, *J. Electron Spectrosc. Relat. Phenom.* **2001**, *119*, 161 – 174; f) L. X. Chen, W. J. H. Jager, G. Jennings, D. J. Gosztola, A. Munkholm, J. P. Hessler, *Science* **2001**, *292*, 262 – 264; g) L. X. Chen, G. Jennings, T. Liu, D. J. Gosztola, J. P. Hessler, D. V. Scaltrito, G. J. Meyer, *J. Am. Chem. Soc.* **2002**, *124*, 10861 – 10867; h) L. X. Chen, G. B. Shaw, I. Novozhilova, T. Liu, G. Jennings, K. Attenkofer, G. J. Meyer, P. Coppens, *J. Am. Chem. Soc.* **2003**, *125*, 7022 – 7034; i) G. B. Shaw, C. D. Grant, H. Shirota, E. W. Castner, G. J. Meyer, L. X. Chen, *J. Am. Chem. Soc.* **2007**, *129*, 2147 – 2160; j) L. X. Chen, X. Y. Zhang, J. V. Lockard, A. B. Stickrath, K. Attenkofer, G. Jennings, D. J. Liu, *Acta Crystallogr. Sect. A* **2010**, *66*, 240 – 251; k) X. F. Qi, P. I. Djurovich, N. C. Giebink, M. E. Thompson, S. R. Forrest, *Chem. Phys. Lett.* **2008**, *458*, 323 – 328; l) E. Borfecchia, C. Garino, L. Salassa, T. Ruiu, D. Gianolio, X. Y. Zhang, K. Attenkofer, L. X. Chen, R. Gobetto, P. J. Sadler, C. Lamberti, *Dalton Trans.* **2013**, *42*, 6564 – 6571; m) D. J. Thiel, P. Livins, E. A. Stern, A. Lewis, *Nature* **1993**, *362*, 40 – 43; n) M. Christensen, K. Haldrup, K. Bechgaard, R. Feidenhans'l, Q. Y. Kong, M. Cammarata, M. Lo Russo, M. Wulff, N. Harrit, M. M. Nielsen, *J. Am. Chem. Soc.* **2009**, *131*, 502 – 508; o) Q. J. Pan, H. G. Fu, H. T. Yu, H. X. Zhang, *Inorg. Chem.* **2006**, *45*, 8729 – 8735; p) I. V. Novozhilova, A. V. Volkov, P. Coppens, *J. Am. Chem. Soc.* **2003**, *125*, 1079 – 1087; q) J. V. Lockard, A. A. Rachford, G. Smolentsev, A. B. Stickrath, X. H. Wang, X. Y. Zhang, K. Atenkoffer, G. Jennings, A. Soldatov, A. L. Rheingold, F. N. Castellano, L. X. Chen, *J. Phys. Chem. A* **2010**, *114*, 12780 – 12787; r) S. Cho, M. W. Mara, X. H. Wang, J. V. Lockard, A. A. Rachford, F. N. Castellano, L. X. Chen, *J. Phys. Chem. A* **2011**, *115*, 3990 – 3996.

[3] M. Han, Y. Tian, Z. Yuan, L. Zhu, B. Ma, *Angew. Chem. Int. Ed.* **2014**, *53*, 10908 – 10912; *Angew. Chem.* **2014**, *126*, 11088 – 11092.

[4] a) S. W. Lai, M. C. W. Chan, K. K. Cheung, S. M. Peng, C. M. Che, *Organometallics* **1999**, *18*, 3991 – 3997; b) A. Chakraborty, J. C. Deaton, A. Haefele, F. N. Castellano, *Organometallics* **2013**, *32*, 3819 – 3829; c) K. W. Wang, J. L. Chen, Y. M. Cheng, M. W. Chung, C. C. Hsieh, G. H. Lee, P. T. Chou, K. Chen, Y. Chi, *Inorg. Chem.* **2010**, *49*, 1372 – 1383; d) A. A. Rachford, F. N. Castellano, *Inorg. Chem.* **2009**, *48*, 10865 – 10867.

[5] a) T. Šolomek, C. G. Bochet, T. Bally, *Chem. Eur. J.* **2014**, *20*, 8062 – 8067; b) S. Roy, S. Goedecker, V. Hellmann, *Phys. Rev. E* **2008**, *77*, 056707.

[6] B. W. Ma, J. Li, P. I. Djurovich, M. Yousufuddin, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2005**, *127*, 28 – 29.

[7] J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055 – 3066.

[8] a) M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, W. de Jong, *Comput. Phys. Commun.* **2010**, *181*, 1477 – 1489; b) W. J. Stevens, M. Krauss, H. Basch, P. G. Jasien, *Can. J. Chem.* **1992**, *70*, 612 – 630; c) W. J. Stevens, H. Basch, M. Krauss, *J. Chem. Phys.* **1984**, *81*, 6026 – 6033; d) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100; e) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[9] K. Saito, Y. Nakao, S. Sakaki, *Inorg. Chem.* **2008**, *47*, 4329 – 4337.

[10] a) S. R. Logan, *J. Chem. Educ.* **1982**, *59*, 279 – 281; b) K. J. Laidler, *J. Chem. Educ.* **1984**, *61*, 494 – 498; c) S. R. Logan, *J. Chem. Educ.* **1999**, *76*, 899 – 899.

Received: June 7, 2015
Revised: June 25, 2015