Tetrahedron 68 (2012) 529-533

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Mechanofluorochromism of carbazole-type D $-\pi$ -A fluorescent dyes

Yousuke Ooyama, Naoya Yamaguchi, Shogo Inoue, Tomoya Nagano, Eigo Miyazaki, Hiroshi Fukuoka, Ichiro Imae, Kenji Komaguchi, Joji Ohshita, Yutaka Harima *

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

ARTICLE INFO

Article history: Received 22 August 2011 Received in revised form 4 November 2011 Accepted 5 November 2011 Available online 17 November 2011

ABSTRACT

We have newly designed and synthesized unsymmetrical carbazole-type $D-\pi-A$ fluorescent dyes. The dyes show a bathochromic shift-type mechanofluorochromism (MFC): grinding of as-recrystallized dyes induces a bathochromic shift of fluorescent color and the fluorescent color is recovered by heating or exposure to solvent vapor. In order to clarify the MFC mechanism for the carbazole-type $D-\pi-A$ fluorescent dyes, time-resolved fluorescence spectroscopy, X-ray powder diffractometry, single-crystal X-ray structural analysis, IR spectroscopy, and differential scanning calorimetry are performed before and after grinding of the solids. On the basis of experimental results and semi-empirical molecular orbital calculations (AM1 and INDO/S), we have revealed that the MFC is attributed to a reversible switching between crystalline and amorphous states with changes of intermolecular hydrogen bonding and $\pi-\pi$ interaction.

© 2011 Elsevier Ltd. All rights reserved.

Tetrahedror

1. Introduction

Since Araki et al. reported mechanofluorochromism (MFC) of amide-substituted tetraphenylpyrene C6TPPy in 2007,¹ the MFC organic dyes, which show a hypsochromic or a bathochromic shift of fluorescent color induced by mechanical stress to the crystal, being accompanied by a reversion to the original fluorescent color by heating or exposure to solvent vapor, have received an increasing interest as attractive materials both for the fundamental research field of solid-state photochemistry and for the applied field of optoelectronic devices.^{2–5} The hypsochromic shift-type MFC of C6TPPy has been explained in terms of a reversible change of intermolecular amide hydrogen bonds by grinding and heating. More recently, Park et al. have found an interesting stimuli luminescence of cyano distrylbenzene derivative DBDCS: a hypsochromic shift of fluorescent color is induced by thermo-stimulus to the as-recrystallized DBDCS, being accompanied by a reversion to the original fluorescent color by mechano-stimulus.⁵ They have demonstrated that the origin for the stimuli luminescence switching is the two-directional shear-sliding capability of molecular sheets, which are formed via intermolecular multiple C–H…N and C-H…O hydrogen bonds. These MFC organic dyes so far reported are symmetrical molecules, and the number of organic fluorescent dyes exhibiting the MFC is still limited and the mechanism is a matter, which requires intensive debates.

In 2009, we have found that newly developed unsymmetrical heteropolycyclic donor–acceptor π -conjugated

 $(D-\pi-A)$ fluorescent dyes with strong electron-withdrawing substituents as acceptor and thus large dipole moments (ca. 5 D) show a bathochromic shift-type MFC.⁶ We have ascribed the MFC to a reversible switching between crystalline and amorphous states with changes of dipole–dipole interaction and intermolecular $\pi-\pi$ interaction.

In order to obtain further useful information on the effects of the substituents and chromophore skeleton on the MFC of unsymmetrical D $-\pi$ –A fluorescent dyes, we have newly designed and synthesized carbazole-type D $-\pi$ –A fluorescent dyes **1** and **2** with a diphenylamino group as D, *p*-pyridine ring as A, a carbazole skeleton as π -conjugated system, and a substituent (R) (Scheme 1, detailed synthesis procedures for the dyes are shown in Supplementary data). Herein, on the basis of experimental results and semi-empirical molecular orbital calculations (AM1 and INDO/S), we discuss the mechanism of bathochromic shift-type MFC of unsymmetrical carbazole-type D $-\pi$ –A fluorescent dyes **1** and **2**.



Scheme 1. Carbazole-type $D-\pi-A$ fluorescent dyes.



^{*} Corresponding author. Tel.: +81 82 424 6534; fax: +81 82 424 5494; e-mail address: harima@mls.ias.hiroshima-u.ac.jp (Y. Harima).

^{0040-4020/\$ –} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2011.11.012

2. Results and discussion

2.1. Photophysical properties of $D-\pi-A$ fluorescent dyes in solution and in the solid-state

The absorption and fluorescence spectra of **1** and **2** in 1.4dioxane are shown in Fig. 1 and their spectral data are summarized in Table 1. The absorption and fluorescence spectra of 1 and 2 resemble very well each other, showing that the effect of N-alkylation of the carbazole ring on the photophysical properties of the dye 1 is negligible. The dyes 1 and 2 show two absorption maxima: one band appears at around 305 nm ascribed to $\pi \rightarrow \pi^*$ transition, and another band occurs at around 375 nm assigned to the intramolecular charge transfer (ICT) excitation from D (diphenylamino group) to A (*p*-pyridine ring). The corresponding fluorescence maximum occurs at around 420 nm and the fluorescence quantum yields ($\Phi_{\rm F}$) are ca. 0.8. The time-resolved fluorescence spectroscopy of **1** and **2** indicated that the decay profile fitted satisfactorily a single exponential function with $\tau_f = 1.9$ ns for both **1** and **2**. Both **1** and 2 in 1,4-dioxane were nearly-colorless, and their fluorescent colors were blue for both **1** and **2**.



Fig. 1. Absorption and fluorescence spectra of 1 and 2 in 1,4-dioxane.

formation of intermolecular $\pi - \pi$ interactions⁷ or continuous intermolecular hydrogen bonding⁸ in the crystalline state leading to delocalization of excitons or eximers.

Table 2

Solid-state photophysical data for 1 and 2 before and after grinding

Dye	Excitation λ ^{ex} _{max} /nm	Excitation λ ^{em} _{max} /nm	$\Phi_{\rm F}{}^{\rm a}$	τ_1/ns^b (A ₁ /%) ^c	$ au_2/{ m ns}^{ m b}$ $(A_2/\%)^{ m c}$
1 (Before)	441	463	0.02	0.2 (41)	2.6 (59)
1 (After)	450	477	0.02	0.2 (79)	4.2 (21)
2 (Before)	397	434	0.17	0.4 (81)	2.2 (19)
2 (After)	424	456	0.16	0.4 (66)	3.6 (34)

^a Fluorescence quantum yield.

^b Fluorescence lifetime.

^c Fractional contribution.



Fig. 2. (a) Solid-state excitation and (b) emission spectra of the crystals of **1** and (c) Solid-state excitation and (d) emission spectra of the crystals of **2**.

Table 1

Spectroscopic properties of 1 and 2 in 1,4-dioxane and calculated absorption spectral data

Compound	In 1,4-Dioxane				Calculation ^c		
	$\lambda_{max}^{abs}/nm \ (\epsilon_{max}/M^{-1} \ cm^{-1})$	λ_{\max}^{fl}/nm	${\Phi_{\mathrm{F}}}^{\mathrm{a}}$	τ_f/ns^b	$\lambda_{\rm max}/{\rm nm}$	$f^{\rm d}$	CI component ^e
1	305 (15,700), 372 (30,200)	423	0.83	1.9	306	0.23	HOMO \rightarrow LUMO+2 (66%)
					345	0.96	HOMO \rightarrow LUMO (65%)
2	304 (18,000), 375 (33,000)	423	0.84	1.9	306	0.25	$HOMO \rightarrow LUMO + 2 (68\%)$
					345	0.87	HOMO→LUMO (61%)

^a Fluorescence quantum yields (ϕ) were determined by using a calibrated integrating sphere system (λ_{ex} =370 nm).

^b Fluorescence lifetime.

^c Calculated at INDO/S method after geometrical optimizations using the MOPAC/AM1 method.

^d Oscillator strength.

^e The transition is shown by an arrow from one orbital to another, followed by its percentage CI (configuration interaction) component.

On the other hand, colors of the dyes recrystallized from acetone were light-yellow for **1** and nearly-colorless for **2**, and the fluorescent colors were blue for both **1** and **2**. The fluorescence excitation and emission maxima (λ_{max}^{ex} and λ_{max}^{em}) of the dyes in the crystalline state were red-shifted by 69 and 40 nm for **1** and 22 nm and 11 nm for **2**, respectively, relative to those for the corresponding dyes in 1,4-dioxane, being accompanied by the considerable decrease in the $\Phi_{\rm F}$ value ('before' in Table 2 and Fig. 2). For D $-\pi$ -A fluorescent dyes, in general, the red-shifts of λ_{max}^{ex} and λ_{max}^{em} , and the lowering of $\Phi_{\rm F}$ value by changing from solution to the crystalline state are quite common and explained in terms of the

2.2. Semi-empirical MO calculations (AM1, INDO/S)

The photophysical properties of **1** and **2** were analyzed by using semi-empirical molecular orbital (MO) calculations. The molecular structures were optimized by using the MOPAC/AM1 method,⁹ and then the INDO/S method¹⁰ was used for spectroscopic calculations. The calculated absorption wavelengths and the transition characters of the absorption bands are collected in Table 1. The calculated absorption wavelengths and the oscillator strength values of the two dyes are comparable to the observed spectra in 1,4-dioxane; the effect of N-alkylation of the carbazole ring on the photophysical

properties of **1** and **2** is negligible, in accord with the experimental results. The calculations indicate that the longest excitation bands are mainly assignable to the transition from HOMO to LUMO, where HOMO is mostly localized on the diphenylamino–carbazole moiety and LUMO is mostly localized on the pyridinyl–carbazole moiety. The HOMO and LUMO of **1** and **2** are shown in Fig. 3a. The changes in the calculated electron density accompanied by the first electron excitation for **1** and **2** are shown in Fig. 3b, which reveal a strong migration of an electron from the diphenylamino–carbazole moiety to the pyridine ring. The values of the dipole moment in the ground state (μ_g) are ca. 3.6 D for both **1** and **2**.



Fig. 3. (a) HOMO and LUMO of **1** and **2**. The red and blue lobes denote the positive and negative phases of the coefficients of the molecular orbitals. The size of each lobe is proportional to the MO coefficient. (b) Calculated electron density changes accompanying the first electronic excitation of **1** and **2**. The black and white lobes signify decrease and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron density change. (Light blue, green, blue and red balls correspond to hydrogen, carbon, nitrogen, and oxygen atoms, respectively.)

2.3. MFC characteristics of D $-\pi$ -A fluorescent dyes

The MFC characteristics of the carbazole-type $D-\pi-A$ fluorescent dyes were investigated according to the following procedure. By grinding the as-recrystallized dyes **1** and **2** at a stress of $50-100 \text{ N/cm}^2$ in a mortar with a pestle, the λ_{max}^{ex} and λ_{max}^{em} for **1** and **2** are red-shifted by 9 nm and 14 nm for **1** and 27 nm and 22 nm for **2**, respectively. However, the Φ_F values change little by grinding. The photophysical data of the two dyes before and after grinding of as-recrystallized dyes are summarized in Table 2 and the excitation and fluorescence spectral changes are also shown in Fig. 2. When the ground samples of **1** and **2** were heated at 150 °C for **1** and 110 °C for **2** (beyond the recrystallization temperature (T_c), described later), respectively, or exposed for several minutes to organic solvents, such as acetone, the colors and fluorescent colors of the dyes recovered to the original ones.

The time-resolved fluorescence spectroscopy with the dyes **1** and **2** revealed that, irrespective of grinding, the fluorescence decay profiles fitted biexponential curves with fluorescence lifetimes of τ_1 =0.2–0.4 ns and τ_2 =2.2–4.2 ns (Table 2). More interestingly, the emission wavelengths (λ_{max}^{trs}) for **1** in the time-resolved measurements were dependent on the time window: for the asrecrystallized dye, 462 nm for 0–4 ns and 517 nm for 5–13 ns; for the ground dye, 475 nm for 0–4 ns and 500 nm for 5–10 ns. For the dye **2**, however, the λ_{max}^{trs} value was independent of the time

window and coincided with the emission wavelength λ_{max}^{em} in the normal fluorescence spectroscopy. The fluorescence decay profiles indicate the existence of two distinct emitting states in both the dyes **1** and **2** before and after grinding.

2.4. Measurements of XRD, DSC, and IR spectra for the solids before and after grinding

The XRD patterns and DSC curves for **1** and **2** before and after grinding of as-recrystallized dyes are shown in Figs. 4 and 5, respectively. The XRD measurements with as-recrystallized dyes **1** and **2** exhibited diffraction peaks ascribable to well-defined microcrystalline structures. They almost disappeared after grinding, showing that the crystal lattice was significantly disrupted. For both the dyes **1** and **2**, the diffraction peaks of the ground dyes after being heated were quite similar to those before grinding, suggestive of recovery of the microcrystalline structure. The DSC analysis for dyes **1** and **2** indicated that the dyes **1** and **2** before grinding showed only one sharp endothermic peak associated with melting. On the other hand, the ground solids underwent an endothermic glass transition (T_g) and then an exothermic recrystallization (T_c) before melting (T_m). The DSC traces of the ground powders are typical of amorphous solids.



Fig. 4. XRD patterns of (a) 1 and (b) 2 before and after grinding, and after heating the ground solids.



Fig. 5. DSC curves (scan rate: 10 °C min⁻¹) of (a) 1 and (b) 2 before and after grinding.

The FT-IR study for the as-recrystallized dye **1** show that no free N–H stretching of carbazole amino group is present, but the broadening of the absorption band at 3417 cm⁻¹ indicates the formation of the weaker hydrogen bondings between the proton on carbazole nitrogen atom and pyridine nitrogen (Fig. 6), which is completely consistent with the X-ray structural analysis of **1** (described later). On the other hand, the N–H stretching of carbazole amino group at 3403 cm⁻¹ observed in the IR spectrum of the ground dye become sharper than that observed in the as-recrystallized dye, indicative of the formation of the stronger hydrogen bonding.



Fig. 6. IR spectra of 1 before and after grinding.

2.5. X-ray crystal structure of D $-\pi$ -A fluorescent dye

A single-crystal X-ray structural analysis was successfully made for 1. As shown in Fig. 7, dye molecules are linked by intermolecular NH…N hydrogen bonds between the proton on carbazole nitrogen atom and pyridine nitrogen to form one-dimensional molecular chain: a proton on carbazole nitrogen atom in the dye molecule is directing toward the pyridine nitrogen of the neighboring dye (N(1)) $H(1)\cdots N(3)^*$ angle=161(1)°, $N(1)\cdots N(3)^*$ distance=2.924(2) Å). There are no short $\pi - \pi$ contacts of less than 3.60 Å between the neighboring fluorophores, which indicates the absence of the $\pi - \pi$ interactions between the fluorophores. The X-ray structural analvsis reveals that the formation of a continuous intermolecular hydrogen bonding between the fluorophores is a principal factor of a large red-shift of the absorption and fluorescence maxima and the drastic solid-state fluorescence quenching for the crystal of 1 from 1,4-dioxane to the solid state.⁸ Unfortunately, we could not obtain sufficient sizes of single crystals for 2 to make the X-ray structural analysis possible, however, the relatively strong fluorescence intensity for the crystal of 2 demonstrated that the N-butylation of carbazole moiety can effectively remove the formation of



Fig. 7. (a) Crystal packing and (b) hydrogen bonding pattern of 1.

a continuous intermolecular hydrogen bonding between the fluorophores, although the formation of intermolecular $\pi - \pi$ interactions between the fluorophores is responsible for the red-shift of the absorption and fluorescence maxima and a decrease in the solid-state fluorescence for **2** from 1,4-dioxane to the crystalline state.

2.6. Mechanism of MFC observed with D $-\pi$ -A fluorescent dyes

In some pigments, the color tone of a pigment powder is known to depend on the size of the particles due to the difference in the degree of light scattering on the pigment surfaces. In the present experiments with the carbazole-type $D-\pi-A$ fluorescent dyes, however, grinding of their powders induces shifts in peak wavelength of fluorescence spectra as well as absorption spectra. These spectroscopic observations rule out the possibility that the change in particle size is responsible for the color and fluorescent color changes observed here. Moreover, the XRD and DSC measurements demonstrate that the carbazole-type D $-\pi$ -A fluorescent dyes interconvert between microcrystalline and amorphous states by grinding and heating. Thus, based on the above results, in the case of the D– π –A fluorescent dyes **1** and **2**, the red-shifts of λ_{max}^{ex} and $\lambda_{\rm max}^{\rm em}$, and lowering of $\Phi_{\rm F}$ by changing from solution to the crystalline state are explained in terms of a continuous intermolecular hydrogen bonding for **1** and the intermolecular $\pi - \pi$ interactions for 2 in the crystalline state. By grinding the solids of 1 and 2, the λ_{max}^{ex} and λ_{max}^{em} are slightly red-shifted. The XRD and DSC measurements demonstrate that the dyes 1 and 2 interconvert between microcrystalline and amorphous states by grinding and heating. Moreover, it was found for the dye 1 that the intermolecular hydrogen bonding for the ground dye becomes stronger than that observed in the as-recrystallized dye. On these bases, it may be inferred that the bathochromic shift-type MFC observed with 1 and **2** by changing from the crystalline state to the amorphous state are caused by the formations of the stronger hydrogen bonding for **1** and intermolecular $\pi - \pi$ interactions for **2** (Fig. 8). Our previous study has demonstrated that a large bathochromic shift-type MFC observed with D– π –A fluorescent dyes (μ g=ca. 5 D) are caused by strong dipole-dipole interactions. Thus, it was suggested that a relatively small MFC for 1 and 2 is ascribable to their weak dipole characters (μ_g =ca. 3.5 D). On the other hand, the Φ_F values undergo very little change from the crystalline state to the amorphous state. This suggests that a non-radiative decay route for the excited states is relatively discouraged by the hydrogen bonding and the $\pi-\pi$ interactions in the amorphous states for this series of $D-\pi-A$ fluorescent dyes.

3. Conclusion

We have found a new class of unsymmetrical carbazole-type D $-\pi$ -A fluorescent dyes displaying a bathochromic shift-type mechanofluorochromism (MFC). This study demonstrates that the MFC of the D $-\pi$ -A fluorescent dyes is attributed to a reversible switching between crystalline and amorphous states with changes of intermolecular hydrogen bonding and π - π interaction before and after grinding. We believe that these mechanofluorochromic dyes can be a promising class of organic fluorescent dyes for rewritable photoimaging and electroluminescence devices.

4. Experimental

4.1. General

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer by ATR method. The load measurement was



Fig. 8. Proposed mechanisms of MFC observed with (a) Carbazole-type D– π –A fluorescent dyes 1 and (b) 2.

performed with IMADA push-pull scale and digital force gauge (ZP-200/V). Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields in solution and in the solid state were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system (λ_{ex} =370 nm). Fluorescence lifetimes were determined with a HAMAMATSU Photonics C4334/C8898 time-resolved spectrophotometer by excitation at 375 nm (laser diode). Powder X-ray diffraction measurements were performed on a Bruker D8 diffractometer with Cu K α radiator. Differential scanning calorimetry of the samples was carried out using a Shimadzu DSC-60.

4.2. Computational methods

The semi-empirical calculations were carried out with the WinMOPAC Ver. 3.9 package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were made using the AM1 method. All geometries were completely optimized (keyword PRECISE) by the eigenvector following routine (keyword EF). Experimental absorption spectra of the compounds were compared with their absorption data by the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic). Dipole moments of the compounds were also evaluated from INDO/S calculations. All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which included the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 225 configurations were considered [keyword CI (15 15)].

4.3. X-ray crystallographic studies

Crystals of **1** were recrystallized from a mixture of $CH_2Cl_2-n_$ hexane as a light-yellow prism, air stable. The one selected had approximate dimensions of 0.80×0.30×0.30 mm. The data sets were collected at 20±1 °C on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using graphite-monochromated Mo Ka $(\lambda = 0.71075 \text{ Å})$ radiation at 50 kV and 40 mA. In all cases, the data were corrected for Lorentz and polarization effects. All calculations were performed using the teXsan¹¹ crystallographic software package of Molecular Structure Corporation. The crystal structure was solved by direct methods using SIR 92.¹² The structures were expanded using Fourier techniques.¹³ All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically and not refined. Compound 1: $C_{29}N_{3}H_{21}$, M=411.51, monoclinic, space group P_{21}/c (no.14), a=7.4450(7), b=28.080(3), c=10.787(1) Å, $\beta=92.211(3)^{\circ}, \beta=92.211(3)^{\circ}, \beta=92.212(3)^{\circ}, \beta=92.211(3)^{\circ}, \beta=92.211(3)^$ V=2253.3(4) Å³, $D_c=1.213$ g cm⁻³, Z=4, 21,242 reflections measured, 5023 unique (R_{int}=0.031). The final R indices were R_1 =0.048, wR=0.161 (I>2 σ (I)), GOF=1.11. Crystallographic data (excluding structure factors) has been deposited with Cambridge Crystallographic Data Centre as supplementary publication number CCDC 810771. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.au.uk/data_request/cif.

Acknowledgements

This work was supported by Grants-in-Aid for Young Scientist (B) (22750179) from the Japan Society for the Promotion of Science (JSPS) and by a research grant from the Mikiya Science and Technology Foundation.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.11.012.

References and notes

- Sagara, Y.; Mutai, T.; Yoshikawa, I.; Araki, K. J. Am. Chem. Soc. 2007, 129, 1520.
 (a) Sagara, Y.; Kato, T. Angew. Chem., Int. Ed. 2008, 47, 1; (b) Sagara, Y.; Kato, T.
- Nature Chem. 2010, 1, 605. 3. Kunzalman, J.; Kinami, M.; Crenshaw, B. R.; Protasiewicz, J. D.; Weder, C. Adv.
- Milizamian, J., Kinami, M., Creisnaw, B. K., Protasiewicz, J. D., Weder, C. Auv. Mater. **2008**, 20, 119.
- 4. Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. J. Am. Chem. Soc. 2010, 132, 2160.
- Yoon, S.-J.; Chung, J. W.; Gierschner, J.; Kim, K. S.; Choi, M.-G.; Kim, D.; Park, S. Y. J. Am. Chem. Soc. 2010, 132, 13675.
- 6. (a) Ooyama, Y.; Kagawa, Y.; Fukuoka, H.; Ito, G.; Harima, Y. Eur. J. Org. Chem. 2009, 31, 5321; (b) Ooyama, Y.; Ito, G.; Fukuoka, H.; Nagano, T.; Kagawa, Y.; Imae, I.; Komaguchi, K.; Harima, Y. Tetrahedron 2010, 66, 7268; (c) Ooyama, Y.; Harima, Y. J. Mater. Chem. 2011, 21, 8372.
- (a) Langhals, H.; Potrawa, T.; Nöth, H.; Linti, G. Angew. Chem., Int. Ed. Engl. 1989, 28, 478; (b) Yeh, H.-C.; Wu, W.-C.; Wen, Y.-S.; Dai, D.-C.; Wang, J.-K.; Chen, C.-T. J. Org. Chem. 2004, 69, 6455; (c) Ooyama, Y.; Okamoto, T.; Yamaguchi, T.; Suzuki, T.; Hayashi, A.; Yoshida, K. Chem.—Eur. J. 2006, 12, 7827.
- (a) Ooyama, Y.; Nakamura, T.; Yoshida, K. New J. Chem. 2005, 29, 447; (b) Ooyama, Y.; Uwada, K.; Kumaoka, H.; Yoshida, K. Eur. J. Org. Chem. 2009, 34, 5979; (c) Ooyama, Y.; Nabeshima, S.; Mamura, T.; Ooyama, H. E.; Yoshida, K. Tetrahedron 2010, 66, 7954.
- Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. J. Am. Chem. Soc. 1985, 107, 3902.
- (a) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973**, 32, 111; (b) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1976**, 42, 223; (c) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, 53, 21.
- 11. teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation 1985 and 1992.
- Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. J. Appl. Crystallogr. 1994, 27, 435.
- DIRDIF94 Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRIF94 Program System, Technical Report* of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.