DOI: 10.1002/chem.201203047



Synthesis and Structure–Property Relationships of 2,2'-Bis(benzo[b]phosphole) and 2,2'-Benzo[b]phosphole–Benzo[b]heterole Hybrid π Systems

Yukiko Hayashi,^[a] Yoshihiro Matano,^{*[a]} Kayo Suda,^[b] Yoshifumi Kimura,^[c] Yoshihide Nakao,^[d] and Hiroshi Imahori^[a, e]

Abstract: The first comprehensive study of the synthesis and structureproperty relationships of 2,2'-bis-(benzo[b]phosphole)s and 2,2'-benzo[b]phosphole-benzo[b]heterole hybrid π systems is reported. 2-Bromobenzo[b]phosphole P-oxide underwent copper-assisted homocoupling (Ullmann coupling) and palladium-catalyzed cross-coupling (Stille coupling) to give new classes of benzo[b]phosphole derivatives. The benzo[b]phospholebenzo[b]thiophene and -indole derivatives were further converted to P,Xbridged terphenylenes (X=S, N) by a palladium-catalyzed oxidative cycloaddition reaction with 4-octyne through the C_{β} -H activation. X-ray analyses of three compounds showed that the benzo[b]phosphole-benzo[b]heterole derivatives have coplanar π planes as a result of the effective conjugation through inter-ring C-C bonds. The π - π^* transition energies and redox potentials of the *cis* and *trans* isomers of bis-(benzo[b]phosphole) *P*-oxide are very close to each other, suggesting that

Keywords: cross-coupling • heterocycles • homocoupling • phospholes • photophysics their optical and electrochemical properties are little affected by the relative stereochemistry at the two phosphorus atoms. The optical properties of the benzo[b]phosphole–benzo[b]heterole hybrids are highly dependent on the benzo[b]heterole subunits. Steady-state UV/Vis absorption/fluorescence spectroscopy, fluorescence lifetime measurements, and theoretical calculations of the non-fused and acetylene-fused benzo[b]phosphole–benzo[b]heterole π systems revealed that their emissive excited states consist of two different conformers in rapid equilibrium.

Introduction

Phosphole, a phosphorus-bridged 1,3-butadiene, is a poorly aromatic heterole with a low-lying LUMO and a narrow LUMO-HOMO gap, which can be finely tuned by chemical functionalizations at the phosphorus center and the ring carbon atoms.^[1] Recently, many efforts have been devoted to the development of arene-fused phosphole π systems for use in materials chemistry.^[2] In particular, benzo[b]phospholes^[3] and related compounds^[4-7] have been receiving increasing attention because they possess rigid and extended π skeletons, which would be beneficial in the molecular design of phosphole-based sensitizers, fluorophores, and semiconductors. The benzo[b]phosphole skeleton contains two functionalization sites, that is, α - and β -carbon atoms, on one side of the phosphole unit. It is therefore important to establish convenient methods for the introduction of π conjugative substituents onto these carbon atoms as well as to systematically understand the optical and electrochemical properties of the resulting benzo[b]phosphole π systems.

The literature to date contains several methodologies for the construction of π -conjugated benzo[*b*]phospholes of types **P1** and **P2** (Scheme 1).^[8] The most frequently studied is the intramolecular cycloaddition of 2-alkynylphenyl-(aryl)phosphine derivatives, which produces benzo[*b*]phospholes bearing α -aryl substituents. The prototype of this re-

- [a] Y. Hayashi, Prof. Dr. Y. Matano, Prof. Dr. H. Imahori Department of Molecular Engineering Graduate School of Engineering Kyoto University, Nishikyo-ku Kyoto 615-8510 (Japan) Fax: (+81)75-383-2571 E-mail: matano@scl.kyoto-u.ac.jp
 [b] K. Suda
- Department of Chemistry Graduate School of Science, Kyoto University Sakyo-ku, Kyoto 606-8502 (Japan)
- [c] Prof. Dr. Y. Kimura Department of Chemical Science and Technology Faculty of Bioscience and Applied Chemistry Hosei University, Tokyo 184-8584 (Japan)
- [d] Prof. Dr. Y. Nakao
 Fukui Institute for Fundamental Chemistry
 Kyoto University, Sakyo-ku
 Kyoto 606-8103 (Japan)
- [e] Prof. Dr. H. Imahori
 Institute for Integrated Cell-Material Sciences (WPI-iCeMS)
 Kyoto University, Nishikyo-ku
 Kyoto 615-8510 (Japan)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201203047.

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Scheme 1. Examples of π -conjugated benzo[*b*]phospholes (E = lone pair, O, S).

action was reported by Winter and Butters in the $1970s^{[9]}$ and has recently been improved by several research groups.^[3] In recent syntheses, Tsuji et al.,^[3a] Sanji et al.,^[3b] and Yamaguchi et al.^[3c] independently achieved the sequential introduction of π -conjugative substituents at the phosphole α - and β -carbon atoms in one-pot or two-step procedures. Yamaguchi et al. also reported the tandem cyclization of 2,2'-bis(diphosphanyl)diphenylacetylene derivatives for the synthesis of **P3** and related compounds.^[6] It is worth noting that some benzo[*b*]phosphole derivatives have exhibited extremely high emitting abilities and/or high electron drift mobilities in the amorphous state.

In the above-mentioned intramolecular cycloaddition methods, the π -conjugative groups are integrated with the starting acetylene substrates in advance. By contrast, in metal-promoted coupling protocols that use halogenated benzo[b]phospholes, the π -conjugative groups can be introduced after construction of the phosphole ring, which enables the divergent synthesis of a variety of 2-arylbenzo[b]phosphole derivatives starting from a common benzo[b]phosphole synthon. To our knowledge, however, metal-promoted coupling reactions have not been fully addressed in the synthesis of 2-arylbenzo[b]phospholes.

In this paper, we report the first examples of 2,2'-bis-(benzo[b]phosphole) and benzo[b]phosphole-benzo[b]heterole hybrid π systems, which were successfully constructed starting from 2-bromobenzo[b]phosphole P-oxide by an Ullmann coupling and a Stille coupling reaction, respectively. In addition, a convenient method for the ring fusion of the benzo[b]phosphole-benzo[b]heterole hybrids was established. The structure-property relationships of the newly prepared benzo[b]phosphole derivatives were investigated by using X-ray crystallography, UV/Vis absorption/fluorescence spectroscopy, cyclic voltammetry, fluorescence lifetime measurements, and theoretical calculations. We investigated 1) the influences of the relative stereochemistry of the bis-(benzo[b]phosphole) P-oxides on their structures and fundamental properties and 2) the effects of the benzo[b]heterole subunits on the optical properties of the non-fused and acetylene-fused benzo[b]phosphole-benzo[b]heterole π systems.

Results and Discussion

Scheme 2 depicts the synthesis of 2-bromobenzo[b]phosphole P-oxide (2),^[10] the starting material in the present coupling reactions. 2-(Trimethylsilyl)benzo[b]phosphole P-



Scheme 2. Regioselective synthesis of 2-bromobenzo[b]phosphole *P*-oxide (2).

oxide (1) was prepared from 1-bromo-1-(trimethylsilyl)styrene according to Kurita's method.^[11] Carbon–silicon bond cleavage in 1 with *N*-bromosuccinimide (NBS) afforded compound 2 in 54% yield. Mathey and coworkers prepared compound 2 in two steps (dibromination–dehydrobromination) from α,β -unsubstituted benzo[*b*]phosphole *P*-oxide; 2 was obtained as a mixture with its regioisomer, the 3-bromo derivative.^[10] The present route from 1 to 2 is promising due to the fact that compound 2 can be prepared as a single regioisomer in a short reaction sequence from the commercially available phenyltrimethylsilylacetylene.

With compound **2** in hand, we first conducted an Ullmann coupling (Scheme 3). Heating a mixture of **2** and metallic copper in DMF for 5 h at 120 °C gave 2,2'-bis-(benzo[b]phosphole) *P*-oxides (*cis*-**3** and *trans*-**3**), together



Scheme 3. Synthesis of the 2,2'-bis(benzo[b]phosphole) derivatives 3 and 4.

with a few byproducts. After column chromatography on silica gel, the major isomer, that is, *cis*-**3** (R_f =0.09, CH₂Cl₂/acetone=5:1), was successfully isolated in 39% yield, but the minor isomer, that is, *trans*-**3** (R_f =0.35), could not be completely separated from the byproducts. Hence, *cis*-**3** was reduced by using HSiCl₃ to the σ^3 -P derivative **4**, which was isolated by column chromatography. The re-oxidation of **4** with H₂O₂ proceeded cleanly and quantitatively to give a mixture of *cis*-**3** and *trans*-**3** in a 2:1 ratio, from which *trans*-**3** was successfully isolated.

The 2,2'-bis(benzo[b]phosphole)s, *cis*-**3**, *trans*-**3**, and the σ^3 -derivative **4** (*cis/trans* mixture), were characterized by using conventional spectroscopic methods. The ³¹P NMR peaks of *cis*-**3** and *trans*-**3** appeared at $\delta_P = 34.9$ and 35.2 ppm, respectively, whereas those of the σ^3 -derivative **4** appeared at $\delta_P = -4.4$ and -4.0 ppm. In the IR spectra, the P=O stretching bands of *cis*-**3** and *trans*-**3** were observed at

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 $\tilde{v}_{max} = 1185$ and 1198 cm^{-1} , respectively, indicating that the multiplicity of the P=O bond in *cis*-**3** is slightly smaller than that in *trans*-**3**. The structure of *cis*-**3** was further elucidated by X-ray crystallography (Figure 1).^[12] Single crystals of *cis*-



Figure 1. Top (left) and side view (right) of *cis*-**3** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and torsion angle [°]: C1–C2 1.357(3), C2–C3 1.472(2), C1–C9 1.452(2), C9–C10 1.352(2), C10–C11 1.4715(19), P1–O1 1.4881(12), P2–O2 1.4892(11), C2-C1-C9-C10 160.76(17).

3, grown from CH₂Cl₂/hexane, were found to be racemic, and the unit cell consists of two kinds of enantiomers. The length of the bond connecting the two phosphole rings is 1.452(2) Å and the torsion angle at the inter-ring linkage is $160.76(17)^\circ$, implying that the two phosphole rings are effectively conjugated. In the packing structure of *cis*-3, (*R*,*R*) and (*S*,*S*) stereoisomers are stacked in parallel and in a head-to-tail orientation with π - π distances of 3.4–3.5 Å (Figure S1 in the Supporting Information).

To examine the optical and electrochemical properties of cis-3 and trans-3, UV/Vis absorption/fluorescence spectra and redox potentials were measured in CH₂Cl₂ (Table 1, Figure 2). It is known that the optical and electrochemical

Table 1. Optical and electrochemical data for the benzo[b] phosphole derivatives.

	$\lambda_{abs} [nm] (\log \varepsilon)^{[a]}$	$\lambda_{ m em} [m nm] (arPsi_{ m f})^{[m a,b]}$	$E_{\rm ox} [V]^{[c]}$	$E_{\rm red} [V]^{[c]}$
2	326 (3.59)	395 (N.d.)	N.d.	N.d.
cis-3	379 (4.25)	441 (0.24)	N.d.	-1.71 (r)
trans-3	380 (4.42)	440 (0.40)	N.d.	-1.67 (r)
5	372 (4.35)	451 (0.22)	N.d.	-1.61 (ir)
6	377 (4.31)	450 (0.17)	+0.98 (ir)	-1.86 (ir)
7	393 (4.07)	542 (0.44)	+0.53 (ir)	-2.00 (ir)
8	344 (3.96)	396 (0.13)	N.d.	N.d.
9	355 (4.08)	431 (0.24)	N.d.	-2.34 (r)

[a] Measured in CH₂Cl₂. [b] Excited at λ_{abs} (excited at 400 nm for the $\Phi_{\rm f}$ measurements). [c] Redox potentials were determined by DPV in CH₂Cl₂ (for **3**, **5**, and **6**) or THF (for **7** and **9**) with 0.1M [Bu₄N][PF₆] (Ag/AgNO₃). First oxidation ($E_{\rm ox}$) and reduction ($E_{\rm red}$) potentials versus the Fc/Fc⁺ couple; r=reversible; ir=irreversible. N.d.=Not determined.

properties of chain-type 2,2'-biphospholes are sensitive to the relative conformations of the two phosphole rings. For example, Hissler and coworkers rationalized the effects of the torsion angles at the inter-ring C–C bonds on the optical properties of a series of methylene-bridged 2,2'-biphosphole derivatives in detail.^[13] As shown in Figure 2, the spectral shapes and the absorption/emission maxima of the present



Figure 2. a) UV/Vis absorption (solid line) and fluorescence (dashed line) spectra of *cis*-**3** and *trans*-**3** in CH₂Cl₂; λ_{ex} =379 (*cis*-**3**) and 380 nm (*trans*-**3**). The fluorescence spectra are normalized for comparison. b) Cyclic voltammograms of *cis*-**3** and *trans*-**3** in CH₂Cl₂ with 0.1 M [*n*Bu₄N][PF₆] as a supporting electrolyte. Scan rate = 60 mV s⁻¹. Asterisks indicate the Fc/Fc⁺ couple.

dimers, cis-3 and trans-3, are very close to each other, except for the extinction coefficients (absorption spectra) and the fluorescence quantum yields (fluorescence spectra). The $\varepsilon_{\rm max}$ and the $\Phi_{\rm f}$ values of *trans*-3 ($\varepsilon_{\rm max}$ =26300 ${\rm M}^{-1}{\rm cm}^{-1}$ $\Phi_{\rm f}$ = 0.40) are higher than the respective values of *cis*-3 $(\varepsilon_{\text{max}} = 17900 \,\text{m}^{-1} \text{cm}^{-1}, \, \Phi_{\text{f}} = 0.24)$. This discrepancy probably stems from the difference in the planarity of cis-3 and trans-3 (see below, torsion angles in Table 2). The small Stokes shifts ($\approx 1000 \text{ cm}^{-1}$) and clear appearance of vibronic structures suggest that the 2,2'-bis(benzo[b]phosphole) frameworks in these dimers are rigid even in solution. In the cyclic voltammetry measurements of cis-3 and trans-3 (in CH_2Cl_2 with 0.1 M [Bu₄N][PF₆] as a supporting electrolyte), reversible first reduction processes were observed at -1.71 and -1.67 V (vs. Fc/Fc+; Fc=ferrocene), respectively. The first reduction potentials (E_{red}) of cis-3 and trans-3 are comparable to those of *cis/trans*-**P2** (E=O, R=Ph; E_{red} =-1.72 and -1.74 V vs. Fc/Fc⁺)^[3c] and cis/trans-P3 (E=O; E_{red} = -1.63 and -1.67 V vs. Fc/Fc⁺)^[6a] reported by Yamaguchi and coworkers (see Scheme 1).

To determine the nature of the frontier orbitals of the 2,2'-bis(benzo[b]phosphole) π systems, we carried out density functional theory (DFT) calculations for *cis*-**3**, *trans*-**3**, and a reference monomer, that is, benzo[b]phosphole *P*-oxide, at the B3LYP/6-31G* level (Table 2 and Figure 3). In the optimized structures, *trans*-**3** (torsion angle (θ)=179.9°) is more planar than *cis*-**3** (θ =159.4°). The C_{β}-C_{β} bond lengths (*a* in Table 2; 1.467–1.468 Å) of *cis*-**3** and *trans*-**3** are slightly shorter than that of the reference monomer (*a*= 1.479 Å), whereas the C_{α}-C_{β} bond lengths (*b* in Table 2; 1.359–1.361 Å) are longer than that of the monomer (*b*=

Table 2.	Bond	lengths	(a-c)	and	torsion	angles	(θ)	of	cis-3,	trans-3,	and
monome	er. ^[a]	-				-					

	Ph O	Ph O ^θ	O Ph	
	monomer ^[a]	cis-3 (X-ray)	cis- 3 ^[a]	trans- 3 ^[a]
a [Å]	1.479	1.47 ^[b]	1.468	1.467
b [Å]	1.345	1.36 ^[b]	1.359	1.361
c [Å]	-	1.45	1.444	1.441
θ [°]	-	160.8	159.4	179.9

[a] Calculated at the B3LYP/6-31G* level. [b] Average values.



Figure 3. HOMOs (bottom) and LUMOs (top) of the reference monomer, *cis*-3, and *trans*-3 and their energies in [eV] calculated at the B3LYP/6-31G* level.

1.345 Å). Obviously, the dimerization of the benzo[b]phosphole units at their α -positions induces effective π conjugation; this is also reflected in the relatively short inter-ring C-C bond length (*c* in Table 2; 1.441–1.444 Å).

As shown in Figure 3, dimerization greatly stabilizes the LUMO and destabilizes the HOMO. As a result, the HOMO–LUMO gap is 1.20–1.26 eV narrower than that of the reference monomer. Furthermore, the orbital diagrams and energies of the HOMO and LUMO of *cis-3* resemble those of *trans-3*, suggesting that the relative stereochemistry at the two phosphorus centers does not significantly affect the orbital nature of the entire bis(benzo[*b*]phosphole) π network.

As expected, bromide **2** underwent a Stille coupling with 2-(tributylstannyl)benzo[b]thiazole, 2-(tributylstannyl)benzo[b]thiophene, and 2-(tributylstannyl)-N-methylindole to give the respective benzo[b]phosphole–benzo[b]heterole hybrid derivatives **5–7** in 48–63 % yields (Scheme 4).

The ³¹P NMR spectra of compounds **5–7** in CD₂Cl₂ showed singlet peaks at $\delta_{\rm P}$ =33.5, 34.3, and 35.5 ppm, respectively. In the ¹H NMR spectrum of compound **7**, the $\beta_{\rm P}$ proton of the phosphole ring appeared downfield ($\delta_{\rm H}$ = 7.52 ppm, $J(\rm P,\rm H)$ =35.6 Hz) relative to that of the pyrrole



Scheme 4. Synthesis of the benzo[b]phosphole-benzo[b]heterole derivatives 5-7 (dba=dibenzylideneacetone).

ring ($\delta_{\rm H}$ = 6.87 ppm), which probably reflects the different electron densities of the heterole subunits; in 7, the phosphole ring is electron deficient, whereas the pyrrole ring is electron rich. In the IR spectra of compounds 5-7, the P=O stretching bands were observed at $\tilde{\nu}_{max} = 1196$, 1195, and 1191 cm⁻¹, respectively. The structures of compounds **5** and 6 were further elucidated by X-ray crystallography. As shown in Figure 4, both 5 and 6 are mostly coplanar with torsion angles at the inter-ring linkages of 175.73(11)° for 5 and 177.27(14)° for 6. In addition, the relatively short interring C-C bond lengths (1.4458(17) Å for 5 and 1.442(2) Å for 6) are responsible for the effective conjugation between the benzo[b]phosphole and the benzo[b]heterole π systems. It is worth noting that both compounds, 5 and 6, are racemic crystals, in which the (R) and (S) stereoisomers make densely π - π stacked pairs in a head-to-tail orientation (Figure S1



Figure 4. Top (left) and side view (right) of a) **5** and b) **6** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: a) C1-C2 1.3524(17), C2-C3 1.4658(18), C1-C9 1.4458(17), P-O 1.4838(8); C2-C1-C9-N 175.73(11). b) C1-C2 1.357(2), C2-C3 1.468(2), C1-C9 1.442(2), C9-C10 1.366(2), C10-C11 1.430(2), P-O 1.4875(10), C2-C1-C9-C10 177.27(14).

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in the Supporting Information) with π - π distances of approximately 3.2-3.3 Å between the two facing thiazolyl rings (for 5) and thiophene rings (for 6). This suggests that the α -heteroaryl rings play an important role in arranging the non-fused benzo[b]phosphole-benzo[b]heterole π systems in the solid state.

The UV/Vis absorption and fluorescence spectra of compounds 5–7 in CH_2Cl_2 are shown in Figure 5 a. Among these three chromophores, the benzo[*b*]phosphole–indole deriva-



Figure 5. UV/Vis absorption spectra (solid line) and fluorescence spectra (dashed line; excited at the absorption maxima) of a) compounds 5–7 in CH_2Cl_2 , b) compound 7 in cyclohexane, benzene, MeCN, and CH_2Cl_2 , and c) compounds 8 and 9 in CH_2Cl_2 .

tive 7 showed the most red-shifted absorption and fluorescence maxima. Furthermore, the Stokes shift of 7 (7000 cm^{-1}) is considerably larger than those of compounds 5 (4950 cm⁻¹) and 6 (4250 cm⁻¹), implying that compound 7 changes its conformational and/or electronic structure in the excited state to a greater extent than compounds 5 and 6. It should also be noted that 7 displays a broad emission band with an emission maximum at 542 nm and a modest fluorescence quantum yield ($\Phi_f=0.44$). In our previous study on chain-type phosphole-heterole-phosphole and heterolephosphole-heterole π systems, we demonstrated that the combination of a phosphole P-oxide (acceptor) and a pyrrole (donor) produced a charge-transfer (CT) character in the excited state.^[14] The large Stokes shift and the broad emission band observed for 7 suggest that the benzo[b]phosphole-indole chromophore possesses considerable CT character in the excited state. Indeed, the fluorescence spectra of 7 exhibited clear solvatochromism (Figure 5b); with increasing solvent polarity, the fluorescence maxima (λ_{em}) are gradually red shifted and the Stokes shifts $(\Delta \tilde{\nu})$ become larger, in the order cyclohexane ($\lambda_{\rm em} = 495 \, \rm nm, \Delta \tilde{\nu} =$ 5020 cm^{-1}) < benzene $(\lambda_{\rm em} = 517 \text{ nm}, \Delta \tilde{\nu} = 5910 \text{ cm}^{-1}) <$ CH₂Cl₂ ($\lambda_{em} = 542 \text{ nm}, \Delta \tilde{\nu} = 7000 \text{ cm}^{-1}$) < MeCN ($\lambda_{em} =$ 542 nm, $\Delta \tilde{\nu} = 7520 \text{ cm}^{-1}$).

As compounds **6** and **7** have two C_{β} -H bonds at the conjugated phosphole and heterole (thiophene or pyrrole) rings, we anticipated that an acetylene unit would be connected at the β -carbon atoms, based on an oxidative cycloaromatization through dual C-H activation. Under the palladium catalysis conditions reported by Jiao and coworkers,^[15] compounds **6** and **7** underwent oxidative coupling with 4-octyne to afford the P,X-bridged (X=S, N) terphenylenes **8** and **9** (Scheme 5). The reaction of **7** proceeded more rapidly than



Scheme 5. Palladium-catalyzed oxidative coupling reaction of compounds 6 and 7 with 4-octyne (Piv=pivalyl).

that of 6, suggesting that an electrophilic C-H activation is involved in the rate-determining step; the C₆-H bond of the more electron-rich pyrrole ring in 7 is easier to activate than that of the thiophene ring in 6. The structures of the new arene-fused phosphole derivatives 8 and 9 were characterized by using conventional spectroscopic techniques. The ³¹P NMR peaks of compounds 8 and 9 were observed upfield ($\delta_{\rm P}$ =27.2–27.7 ppm) compared to those of the precursors 6 and 7 ($\delta_P = 34.3 - 35.5$ ppm). The UV/Vis absorption and fluorescence spectra of the acetylene-fused derivatives 8 and 9 were significantly blue shifted relative to those of the respective non-fused derivatives 6 and 7 (Figure 5c). It should also be noted that the Stokes shifts of compounds 8 (3820 cm^{-1}) and 9 (4810 cm^{-1}) are appreciably smaller than those of 6 (4250 cm⁻¹) and 7 (7000 cm⁻¹), respectively. This demonstrated the rigidity of the fused π frameworks in 8 and 9. Compound 9 also showed a solvatochromic behavior in solution.[16]

To compare the characters of the HOMOs and LUMOs of the benzo[b]phosphole–benzo[b]heterole hybrid π systems, we first performed DFT calculations for compounds **5–7**, **8m**, and **9m** (models for compounds **8** and **9**, respectively; two *n*-propyl groups were replaced by two methyl groups) at the B3LYP/6-31G* level. As shown in Figure 6, both the HOMO and the LUMO levels rise in the order **5**< **6**<**7**, which basically reflects the electron-donating and elec-

as a fluorescence detector. The fluorescence decay curves of compounds **8** and **9** in CH₂Cl₂ were fitted as a single exponential with lifetimes ($\tau_{\rm f}$) of 2.2 and 7.9 ns, respectively. From the $\Phi_{\rm f}$ and $\tau_{\rm f}$ values, the radiative and non-radiative decay rate constants ($k_{\rm r}$ and $k_{\rm nr}$) were determined to be $k_{\rm r}$ = 5.9×10^7 and $k_{\rm nr}$ = 4.0×10^8 s⁻¹ for **8** and $k_{\rm r}$ = 3.0×10^7 and $k_{\rm nr}$ = 9.7×10^7 s⁻¹ for **9**. In contrast, the fluorescence decay curves of the non-fused derivatives **5**–**7** under the same



Figure 6. HOMOs and LUMOs of compounds **5–7**, **8m**, and **9m** and their energies in [eV] calculated at the B3LYP/6-31G* level.

tron-accepting ability of the thiazole, thiophene, and pyrrole rings. The HOMO–LUMO gaps decrease in the order 5 > 6 > 7. Among these three π systems, the inclination of the molecular orbital coefficients for the HOMOs and LUMOs is most distinct for compound 7; the HOMO is mainly localized on the indole unit, whereas the LUMO is mainly localized on the benzo[b]phosphole unit. The calculated orbital diagrams explain the distinct CT character of 7 in its excited state. The acetylene fusion from 6/7 to 8m/9m widens the HOMO–LUMO gap of the benzo[b]phosphole–benzo[b]heterole π systems, which agrees well with the experimentally observed results. In the entirely fused π systems 8m and 9m, the HOMOs essentially possess the character of the dibenzo[b,d]thiophene and carbazole, respectively.

Most of the π -conjugated benzo[*b*]phosphole derivatives have been reported to be fluorescent. To our knowledge, however, little information is available for the photodynamics of this class of compounds. To obtain a deep insight into the effects of the rotation of the inter-ring C–C bond on the photophysical behavior of the present benzo[*b*]phosphole– benzo[*b*]heterole hybrid π systems, we measured the fluorescence lifetimes of the non-fused derivatives **5–7** and the acetylene-fused derivatives **8** and **9** by using a streak camera measurement conditions were analyzed by using two-exponential decay fittings. Figure 7 a shows the fluorescence spectra of 7 in CH₂Cl₂ at different delay times ($\lambda_{ex} = 390$ nm). The fluorescence line shape is dependent on the delay time, suggesting that there are different species in the electronic excited state. Figure 7b shows the changes in the fluorescence intensities of compound 7 in CH₂Cl₂ monitored at 460 and 630 nm. The fluorescence intensity at 460 nm shows a fast decay component following a slow decay component, whereas the fluorescence intensity at 630 nm shows fast rise and slow decay components. The fast decay-time constant of the



Figure 7. a) Time-resolved fluorescence spectra (from 440–640 nm) at 0.1, 5, 10, and 15 ns, and b) time profiles at 460 and 630 nm of the fluorescence decay for **7** in CH₂Cl₂. λ_{ex} = 390 nm.

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460 nm intensity matches the rise-time constant of the 630 nm intensity well. Detailed analysis of the time-resolved fluorescence spectra by using the singular value decomposition (SVD) indicated that there are two emitting species in the electronic excited state and that there is an equilibrium between them (see the Experimental Section). The fact that the acetylene-fused derivatives 8 and 9 obeyed first-order kinetics may suggest that the two emitting species of 5–7 are probably formed through rotation at the inter-ring bond between the phosphole and adjacent heterole rings. A plausible scheme is shown in Figure 8.



Figure 8. Plausible scheme for the photodynamics of 7; r=radiative decay, nr=nonradiative decay.

If we assume that the rate constants of the equilibria in the excited states (k_{AB}, k_{BA}) are larger than those of the sum of the radiative and non-radiative decays from the two excited states $(k_1, k_2; k_1=k_{r1}+k_{nr1}, k_2=k_{r2}+k_{nr2})$, the observed rate constants (k_{fast}, k_{slow}) can be estimated by using Equations (1) and (2) (for details, see the Experimental Section).

$$k_{\text{fast}} = k_{\text{AB}} + k_{\text{BA}} \tag{1}$$

$$k_{\text{slow}} = \frac{k_1 k_{\text{AB}} + k_2 k_{\text{BA}}}{k_{\text{AB}} + k_{\text{BA}}} \tag{2}$$

The k_{fast} and k_{slow} values of compounds 5–7 in CH₂Cl₂ determined by SVD analyses of the time-resolved spectra (Figure S2 in the Supporting Information) are summarized in Table 3. The k_{fast} values thus obtained $(0.55-1.47 \times 10^9 \text{ s}^{-1})$ are four to five times larger than the k_{slow} values $(1.3-3.0 \times 10^8 \text{ s}^{-1})$. The k_{fast} value is directly related to the equilibrium rate constants, whereas the k_{slow} value essentially reflects the fluorescence decay rate constants. As mentioned above, compound 7 exhibited clear solvatochromism in the steady-state fluorescence spectra. The fluorescence decay of 7 was

Table 3. Decay rate constants for **5–7** in various solvents.^[a]

	5 CH ₂ Cl ₂	6 CH ₂ Cl ₂	7 C ₆ H ₆	CH_2Cl_2	MeCN
$c_{\rm fast} [{ m ns}^{-1}]$	1.47	1.29	0.33	0.55	1.03
$c_{\rm slow} [{ m ns}^{-1}]$	0.30	0.14	0.14	0.13	0.16

[a] Determined by the SVD analyses.

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therefore also monitored in benzene and in MeCN. The k_{fast} value increases with an increasing solvent polarity $(3.3 \times 10^8 \text{ s}^{-1} \text{ in benzene}, 10.3 \times 10^8 \text{ s}^{-1} \text{ in MeCN})$, whereas the k_{slow} values are largely independent of the solvent polarity $(1.4 \times 10^8 \text{ s}^{-1} \text{ in benzene}, 1.6 \times 10^8 \text{ s}^{-1} \text{ in MeCN})$. It seems likely that the two emitting species possess different CT characters; the more stable species seems to be more polarized.

Again, it should be noted that the two emitting species presumably arise from rotation at the inter-ring C-C bond, that is, a change in the anti-syn conformations in the excited state. To evaluate the validity of this interpretation, we next performed DFT calculations on compounds 5-7 by using the B3LYP/cc-pVDZ method. In the ground state of 7 (Figure 9a), two conformers, syn ($\theta = 49.5^{\circ}$; θ is the P-C-C-N torsion angle) and *anti* ($\theta = 201.8^{\circ}$), are both energy minima. This trend is similar to the theoretical prediction for the rotational potential energies of 2,5-bis(2-thienyl)phosphole reported by Réau, and coworkers.^[17] The energy differences between the two conformers of 7 $(E_{anti}-E_{syn})$ are 1.5 kcal mol⁻¹ in a vacuum and -0.2 kcalmol⁻¹ in CH_2Cl_2 as determined by using a polarizable continuum model (PCM), indicating that the solvent effect on the anti conformer is more distinct than on the syn conformer. This is probably because the dipole moment of the anti conformer (5.37 D) is larger than that of the syn conformer (3.31 D). The small rotational energy barriers between the two conformers (3-4 kcal mol^{-1}) suggest that rotation occurs freely in the ground state of compound 7. In other words, both conformers are likely to be present in solution. The HOMOs and LUMOs at the different torsion angles and their orbital energies are summarized in Figure S3 in the Supporting Information. It is evident that the electron densities are localized at the twisted structures. In the ground states of compounds 5 and 6, the syn and anti conformers are energy minima with an energy difference of 0.6 kcalmol⁻¹ for **5** and 2.0 kcalmol⁻¹ for 6 (Figure S4 in the Supporting Information). The activation energies of the rotation at the inter-ring C-C bonds are 5–6 kcalmol⁻¹ for **5** and 4–6 kcalmol⁻¹ for **6** (determined in CH₂Cl₂ by using PCM), which implies that the two conformers of 5 and 6 are also in rapid equilibrium in solution.

In the lowest excited singlet (S_1) state of 7 (Figure 9b), the syn conformer ($\theta = 14.8^{\circ}$) is a global minimum, and the anti conformer ($\theta = 212.1^{\circ}$) is a local minimum; the syn conformer is more stable by 1.5 kcalmol⁻¹ than the anti conformer. The rotational energy barriers of 3-6 kcalmol⁻¹ imply that an equilibrium between the two conformers is possible in the S_1 state of 7. The emission energies from the S_1 state of 7 were calculated by considering vertical transitions to the S_0 state at the same geometries. As shown in Figure 9c, the oscillator strengths (f) are highly dependent on the θ values and nearly equal to zero at $\theta = 90$ and 270° (f=0.002-0.005). Apparently, the perpendicularly aligned conformers of 7 are non-fluorescent in nature. At the two energy minima at $\theta = 14.8$ and 212.1° , the S₁-to-S₀ transition energies are $\Delta E = 2.13 \text{ eV}$ (f=0.544) and $\Delta E = 2.16 \text{ eV}$ (f= 0.357), respectively.



Figure 9. Dependences of the P-C-C-N torsion angles (θ [°]) of 7 on a) the relative energies (*E* [kcalmol⁻¹]) in the S₀ state in vacuum and in CH₂Cl₂, b) the relative energies (*E* [kcalmol⁻¹]) in the S₁ state in CH₂Cl₂, and c) the S₁-to-S₀ vertical transition energies (ΔE [eV]) and the oscillator strengths (*f*) in CH₂Cl₂ calculated at the B3LYP/cc-pVDZ level.

Although the calculated transition energies do not completely match the observed ones, the theoretical results indicate that the two emission processes are conceivable after rapid equilibrium between the *syn* and *anti* conformers of **7** in the excited state. Presumably the *trans* conformer (CT^*_A in Figure 8) is converted to the *cis* conformer (CT^*_B) in the S₁ state, followed by dual emissions with different rates at the two different wavelengths.^[18] The local and global minima of the excited states of compounds **5** and **6** were also determined at the same level of calculations. As listed in Table 4, the energy differences between the *syn* and *anti*

Table 4.	Calculated	parameters	at	the S ₀	and S ₁	states	of	5-7.	[a]
							_		

	-						
	5			6	7		
conformation	syn	anti	syn	anti	syn	anti	
$\theta(S_0) [\circ]^{[b]}$	12.5	175.3	26.2	193.5	49.5	201.8	
$E(S_0)$ [kcal mol ⁻¹] ^[c]	0.00	-0.65	0.00	-2.01	0.00	-0.18	
$\theta(S_1)$ [°] ^[d]	0.4	178.0	1.8	185.6	14.8	212.1	
$E(S_1) [kcal mol^{-1}]^{[e]}$	0.00	-0.01	0.00	+0.11	0.00	+1.49	
$\Delta E(S_1 - S_0) [eV]^{[f]}$	2.37	2.41	2.29	2.40	2.13	2.16	
$f(S_1 - S_0)^{[g]}$	0.833	0.851	0.757	0.892	0.544	0.357	

[a] Calculated at the B3LYP/cc-pVDZ level by using the PCM model (CH₂Cl₂). [b] P-C-C-X torsion angles (X=S for **5** and **6**, X=N for **7**) at the local and global minima of the S₀ state. [c] Relative energies of the *syn* and *anti* conformers of the S₁ state. [e] Relative energies of the *syn* and *anti* conformers of the S₁ state. [e] Relative energies of the *syn* and *anti* conformers of the S₁ state. [f] S₁–S₀ vertical transition energies from the local and global minima of the S₁ state. [g] Oscillator strengths of the S₁–S₀ vertical transitions from the local and global minima of the S₁ state.

conformers are 0.01 kcalmol⁻¹ for **5** and 0.11 kcalmol⁻¹ for **6**. The calculated S₁-to-S₀ transition energies from the two energy minima are $\Delta E = 2.37 \text{ eV}$ (f=0.833 at $\theta=0.4^{\circ}$) and $\Delta E = 2.41 \text{ eV}$ (f=0.851 at $\theta=178.0^{\circ}$) for **5** and $\Delta E = 2.29 \text{ eV}$ (f=0.757 at $\theta=1.8^{\circ}$) and $\Delta E = 2.40 \text{ eV}$ (f=0.892 at $\theta=185.6^{\circ}$) for **6**. The emission energies of **5** and **6** are appreciably larger than those of **7**, which is in good agreement with the experimental observations. This may be a result of the different CT characters in their excited states.

Conclusion

We have established new divergent methods for the synthesis of 2,2'-bis(benzo[b]phosphole) and 2,2'-benzo[b]phosphole–benzo[b]heterole π systems based on Ullmann and Stille coupling reactions of 2-bromobenzo[b]phosphole *P*-oxide. The benzo[b]phosphole–benzo[b]heterole π conjugates bearing C_β–H bonds were further converted to P,X-bridged terphenylenes (X = S, N) by palladium-catalyzed oxidative cyclization with 4-octyne through dual C–H activation. These results unambiguously corroborate that metal-promoted coupling reactions are highly promising for introducing π -conjugative functionalities onto the phosphole ring of the benzo[b]phosphole skeleton. The relative stereochemistry at the phosphorus centers was found to have small impacts on the optical and electrochemical properties of the

Chem. Eur. J. 2012, 18, 15972-15983

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bis(benzo[b]phosphole) π systems. In contrast, the optical properties of the benzo[b]phosphole–benzo[b]heterole π conjugates are highly dependent on the combination of benzo[b]heterole subunits. In particular, the benzo[b]phospholeindole derivative exhibits intrinsic CT character in the excited state. Time-resolved fluorescence lifetime measurements and DFT calculations of both the ground state and the excited state of the benzo[b]phosphole–benzo[b]heterole hybrid π systems revealed that two kinds of conformers are formed in rapid equilibrium, with small rotational barriers. Further studies on the application of this class of compounds to organic devices are now in progress.

Experimental Section

All melting points were recorded on a Yanagimoto micro melting point apparatus and are uncorrected. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were measured on a JEOL EX400, AL300, or ECA-600P spectrometer. Chemical shifts are reported as the relative values versus the signal of tetramethylsilane ($^1\!H,\,^{13}\!C)$ or H_3PO_4 ($^{31}P).$ Selected $^1\!H$ NMR spectra are shown in Figures S5-S12 in the Supporting Information. ¹H-¹H COSY spectra were measured on a JEOL ECA-600P spectrometer. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight mass spectra (TOF) were measured on a Shimadzu Biotech AXIMA-CFR spectrometer by using CHCA as a matrix. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific orbitrapXL spectrometer for MALDI, JEOL JMS-SX102A spectrometer for EI and Thermo Fisher Scientific EXACTIVE spectrometer for ESI measurements. IR spectra were obtained on a Thermo Fisher Scientific NICOLET 6700 FTIR spectrometer. UV/Vis absorption and fluorescence spectra were obtained on a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer and on a Horiba FluoroMax-3 spectrometer, respectively. Quantum yield measurements were performed on a Hamamatsu Photonics Quantaurus-QY spectrometer. Electrochemical measurements were performed on a CH Instruments model 660A electrochemical workstation by using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ [0.01 M AgNO₃, 0.1 M [nBu₄N][PF₆] (MeCN)] reference electrode. The potentials were calibrated with ferrocene/ferrocenium. Tetrahydrofuran and diethyl ether (Et2O) were distilled from sodium benzophenone ketyl before use. Compound 1 was prepared according to the reported procedures.^[11] Other chemicals and solvents were of reagent grade quality and used without further purification unless otherwise noted. Thin-layer chromatography was performed with silica gel 60 F254 (Merck), and preparative column chromatography was performed by using ultra pure silica gel (230-400 mesh; SiliCycle Inc). All reactions were performed under an argon atmosphere unless otherwise noted.

Synthesis and characterization of compounds 2-9

Compound **2**: NBS (1.118 g, 6.28 mmol) was added to a solution of compound **1** (0.894 g, 3.00 mmol) in MeCN (26 mL). The resulting mixture was stirred for 5.5 h at room temperature and water was then added. The aqueous layer was extracted with EtOAc and the organic combines were washed with an aqueous saturated solution of Na₂S₂O₃ and brine. The organic layer was dried over Na₂SO₄ and evaporated. The residue was subjected to silica gel column chromatography (CHCl₃/acetone = 20:1). The purple fluorescent fraction (R_f =0.33) was collected and evaporated to give compound **2**^[10] (0.491 g, 54%) as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ =7.30–7.39 (m, 2H), 7.43–7.52 (m, 3H), 7.47 (d, *J*= 28.8 Hz, 1H), 7.58 (t, *J*=8.8 Hz, 1H), 7.63 (dd, *J*=7.3, 10.2 Hz, 1H), 7.72 ppm (dd, *J*=7.8, 12.7 Hz, 2H); ³¹P[¹H] NMR (CDCl₃, 162 MHz): δ = 30.7 ppm.

Compound cis-3: Copper powder was washed with HCl in acetone, followed by acetone alone in advance. The copper powder (0.467 g, 7.3 mmol) was added to a solution of 2-bromobenzo[*b*]phosphole (2) (2.01 g, 6.6 mmol) in DMF (28 mL) at room temperature and the result-

ing mixture was stirred for 4.5 h at 120 °C. The insoluble copper powder in the mixture was filtered off through a Celite bed and water was then added. The aqueous layer was extracted with toluene and the organic combines were washed with brine, dried over Na2SO4, and evaporated. The residue was subjected to silica gel column chromatography (CH2Cl2/ acetone = 5:1). The blue fluorescent fraction (R_f = 0.09) was collected and evaporated to give cis-2,2'-bis(benzo[b]phosphole) P-oxide (cis-3) (0.584 g, 39%) as a yellow solid. In this coupling, trans-3 was also formed but could not be purified by column chromatography. M.p. 277-279°C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.29-7.52$ (m, 17H), 7.57 (dd, J=8.3, 8.3 Hz, 2H), 7.74 ppm (d, J=34.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): $\delta = 125.6$ (t, J = 4.5 Hz), 128.9 (d, J = 6.6 Hz), 129.0 (d, J = 4.9 Hz), 129.3 (dd, J = 10.7, 92.2 Hz), 129.7 (pseudo t, J = 5.8 Hz), 130.5 (pseudo t, J=5.4 Hz), 131.9 (dd, J=4.9, 115.3 Hz), 132.0 (d, J=100.8 Hz), 132.3, 133.4, 140.0 (pseudo t, J=11.9 Hz), 141.8 ppm (pseudo t, J = 13.6 Hz; ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 34.9 \text{ ppm}$; IR (neat): $\tilde{v}_{\text{max}} = 1185 \text{ cm}^{-1}$ (P=O); HRMS (MALDI): m/z calcd for $C_{28}H_{21}O_2P_2$: 451.1011; found: 451.1003 [*M*+H⁺].

Compound 4: HSiCl₃ (2.5 mL, 25 mmol) was added to a solution of *cis*-3 (0.277 g, 0.62 mmol) in toluene (23 mL). After stirring for 19 h at 110 °C, the mixture was added into water and the insoluble white substances were filtered off. The organic layer of the filtrate was separated, and the aqueous layer was extracted with toluene. The organic combines were evaporated. The residue was recrystallized from MeOH/CH₂Cl₂ to give compound 4 as a pale yellow solid (0.116 g, 45%). M.p. 273–275 °C (decomp); ¹H NMR (400 MHz, CDCl₃): δ =7.10–7.52 ppm (m, 20H); ³¹P[¹H] NMR (162 MHz, CDCl₃): δ =-4.41, -3.96 ppm; HRMS (EI): *m*/*z* calcd for C₂₈H₂₀P₂: 418.1040; found: 418.1048 [*M*⁺].

Compound trans-3: An aqueous solution of H2O2 (30%, 3 mL) was added to a solution of compound 4 (86 mg, 0.21 mmol) in CH2Cl2 (30 mL) and the resulting mixture was stirred for 1.5 h at room temperature. The mixture was quenched with an aqueous solution of Na2SO3 (20%, 120 mL) and the organic layer was separated. The aqueous layer was extracted with CH2Cl2 and the organic combines were washed with brine, dried over MgSO₄, and evaporated. The residue was subjected to silica gel column chromatography (CH₂Cl₂/acetone=5:1). The fraction of $R_{\rm f}$ =0.35 was collected and evaporated to give *trans*-3 (6 mg, 12%). M.p. > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.31–7.36 (m, 4 H), 7.45– 7.57 (m, 12H), 7.77 ppm (dd, J=8.3, 12.7 Hz, 4H); ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 35.2 \text{ ppm}$; IR (neat): $\tilde{\nu}_{max} = 1198 \text{ cm}^{-1}$ (P=O); HRMS (EI): m/z calcd for C₂₈H₂₀O₂P₂: 450.0939; found: 450.0935 [M⁺]. Compound 5: A mixture of compound 2 (601 mg, 1.97 mmol), 2-(tributylstannyl)benzothiazole ($\approx 3.0 \text{ mmol}$), and $[Pd(PPh_3)_4]$ (254 mg, 0.220 mmol) in toluene (90 mL) was stirred for 13 h at 110 °C. The aqueous layer was extracted with EtOAc and the organic combines were dried over Na₂SO₄, filtered off through a Celite bed, and evaporated. The residue was subjected to silica gel column chromatography (CH₂Cl₂/ acetone = 10:1). The blue fluorescent fraction $(R_f = 0.31)$ was collected, evaporated, and recrystallized from CH2Cl2/hexane to give compound 5 (341 mg, 48%) as a yellow solid. M.p. 257-259°C (decomp); ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 7.37-7.54$ (m, 6 H), 7.57 (d, J = 6.8 Hz, 1 H), 7.61 (d, J = 7.3 Hz, 1H), 7.69 (dd, J = 8.3, 8.5 Hz, 1H), 7.81 (dd, J = 13.2, 10.0 Hz, 2 H), 7.88 (d, J=7.8 Hz, 1 H), 8.00 (d, J=7.8 Hz, 1 H), 8.02 ppm (d, J = 32.7 Hz, 1 H); ${}^{13}C[{}^{1}H]$ NMR (75 MHz, CD₂Cl₂): $\delta = 122.0$, 123.9, 126.3, 126.6 (d, J = 9.2 Hz), 126.9, 129.2 (d, J = 12.3 Hz), 129.7 (d, J =9.9 Hz), 129.9 (d, J = 102.4 Hz), 131.1 (d, J = 10.5 Hz), 131.5 (d, J =11.1 Hz), 132.9 (d, J=3.1 Hz), 133.8 (d, J=1.8 Hz), 134.6 (d, J=95.0 Hz), 134.8 (d, J = 72.8 Hz), 140.8, 141.2, 143.8 (d, J = 17.9 Hz), 154.2, 160.9 ppm (d, J = 11.7 Hz); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): $\delta =$ 33.5 ppm; IR (neat): $\tilde{v}_{max} = 1196 \text{ cm}^{-1}$ (P=O); HRMS (ESI): *m*/*z* calcd for C₂₁H₁₅NOPS: 360.0606; found: 360.0591 [M+H⁺]; elemental analysis calcd (%) for C₂₁H₁₄NOPS: C 70.18, H 3.93, N 3.90, S 8.92, P 8.62; found: C 70.04, H 3.91, N 3.79, S 8.86, P 8.43.

Compound **6**: A mixture of $[Pd_2(dba)_3]$ (18 mg, 0.020 mmol), (2-furyl)₃P (32 mg, 0.14 mmol), and *N*-methylpyrrolidone (NMP) (1.6 mL) was stirred for 1 h at room temperature. Compound **2** (201 mg, 0.66 mmol), 2-(tributylstannyl)benzo[*b*]thiophene (0.30 mL, 0.84 mmol), NMP (6.4 mL), and CuI (148 mg, 0.78 mmol) were added to this mixture and the result-

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ing mixture was stirred for 14 h at room temperature. A saturated aqueous solution of NH4Cl was then added and insoluble substances were filtered off through a Celite bed. The organic layer was separated and the aqueous layer was extracted with EtOAc/hexane (1:1). The organic combines were washed with water, dried over Na2SO4, and evaporated. The residue was subjected to silica gel column chromatography (CH₂Cl₂/acetone=15:1 to 10:1). The blue fluorescent fraction ($R_{\rm f}$ =0.63 at CH₂Cl₂/ acetone=10:1) was collected, evaporated, and recrystallized from CH₂Cl₂/hexane to give compound 6 (127 mg, 54%) as a yellow solid. M.p. 206–207 °C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.28-7.80$ (m, 14H), 7.51 ppm (d, J=41.5 Hz, 1H); ${}^{13}C{}^{1}H$ NMR (100 MHz, CD₂Cl₂): $\delta = 122.5$, 124.7, 125.1 (d, J = 11.5 Hz), 125.4 (d, J = 9.9 Hz), 126.0, 129.3 (d, J=10.7 Hz), 129.4 (d, J=12.3 Hz), 129.7 (d, J=10.7 Hz), 130.3 (d, J=99.6 Hz), 131.1 (d, J=10.7 Hz), 133.0 (d, J=7.8 Hz), 132.9, 133.0 (d, J=107.8 Hz), 133.8, 134.3 (d, J=93.9 Hz), 136.7 (d, J=14.8 Hz), 137.0 (d, J=2.5 Hz), 137.2 (d, J=2.5 Hz), 139.6, 140.5, 142.1 ppm (d, J= 27.2 Hz); ${}^{31}P{}^{1}H$ NMR (162 MHz, CD₂Cl₂): $\delta = 34.3$ ppm; IR (neat): $\tilde{\nu}_{max} = 1195 \text{ cm}^{-1}$ (P=O); HRMS (ESI): m/z calcd for C₂₂H₁₆OPS: 359.0654; found: 359.0640 [M+H+]; elemental analysis calcd (%) for C22H15OPS: C 73.73, H 4.22, S 8.95, P 8.64; Found: C 73.83, H 4.22, S 8.89, P 8.44.

Compound 7: A mixture of [Pd₂(dba)₃] (18 mg, 0.02 mmol), (2-furyl)₃P (36 mg, 0.16 mmol), and NMP (1.6 mL) was stirred for 1 h at room temperature. Compound 2 (201 mg, 0.66 mmol), N-methyl-2-(tributylstannyl)indole (0.30 mL, 0.65 mmol), NMP (6.4 mL), and CuI (142 mg, 0.75 mmol) were added to this mixture and the resulting mixture was stirred for 3.5 h at room temperature. A saturated aqueous solution of NH_4Cl was then added and insoluble substances were filtered off through a Celite bed. The organic layer was separated, and the aqueous layer was extracted with EtOAc/hexane (1:1). The organic combines were washed with water, dried over Na2SO4, and evaporated. The residue was subjected to silica gel column chromatography (CH2Cl2/acetone=10:1). The yellow fluorescent fraction ($R_{\rm f}$ =0.41) was collected, evaporated, and recrystallized from CH₂Cl₂/hexane to give compound 7 (147 mg, 63%) as a yellow-green solid. M.p. 172-173°C (decomp); ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 3.93$ (s, 3H), 6.87 (s, 1H), 7.05 (dd, J = 6.8, 7.6 Hz, 1H), 7.23 (dd, J=6.8, 7.6 Hz, 1 H), 7.32 (d, J=8.3 Hz, 1 H), 7.35-7.42 (m, 3 H),7.46-7.58 (m, 4H), 7.52 (d, J=35.6 Hz, 1H), 7.62 (dd, J=7.8, 8.3 Hz, 1H), 7.74 ppm (dd, J=8.3, 13.7 Hz, 2H); ${}^{13}C[{}^{1}H]$ NMR (100 MHz, CD₂Cl₂): δ=32.5, 105.9 (d, J=3.3 Hz), 109.8, 120.4, 121.5, 123.6, 125.3 (d, J=9.9 Hz), 127.9, 129.3 (d, J=19.8 Hz), 129.3 (d, J=12.3 Hz), 129.4 (d, J = 19.8 Hz), 130.8 (d, J = 112.0 Hz), 131.1 (d, J = 10.7 Hz), 131.9 (d, J = 10.7 Hz), 67.5 Hz), 132.7 (d, J=2.5 Hz), 133.0 (d, J=16.5 Hz), 133.7 (d, J=1.6 Hz), 136.0 (d, J=18.1 Hz), 139.8, 142.4, 142.7 ppm; ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 35.5$ ppm; IR (neat): $\tilde{\nu}_{max} = 1191$ cm⁻¹ (P=O); HRMS (ESI): *m*/*z* calcd for C₂₂H₁₉NOP: 356.1199; found: 356.1184 [*M*+H⁺].

Compound 8: A mixture of compound 6 (60 mg, 0.17 mmol), 4-octyne (0.12 mL, 0.81 mmol), Pd(OAc)₂ (14 mg, 0.060 mmol), K₂CO₃ (8 mg, 0.06 mmol), tetrabutylammonium bromide (27 mg, 0.085 mmol), and pivalovl alcohol (0.020 mL, 0.17 mmol) in DMF (3 mL) was stirred for 9 d at 100-120 °C under an oxygen atmosphere. The mixture was then diluted with EtOAc/hexane (1:1) and insoluble substances were filtered off through a Celite bed. The aqueous layer was extracted with EtOAc/ hexane (1:1), and the organic combines were washed with water, dried over MgSO₄, and evaporated. The residue was subjected to silica gel column chromatography ($CH_2Cl_2/acetone = 20:1$). The purple fluorescent fraction $(R_{\rm f}=0.24)$ was collected and evaporated to give compound 8 (11 mg, 14%) as an orange solid. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 1.26$ (t, J=7.3 Hz, 3H), 1.27 (t, J=7.3 Hz, 3H), 1.80-1.89 (m, 4H), 3.22-3.27 (m, 2H), 3.33-3.37 (m, 2H), 7.36-7.41 (m, 2H), 7.42-7.53 (m, 4H), 7.64-7.71 (m, 3H), 7.76 (dd, J=7.3, 11.2 Hz, 1H), 7.83 (d, J=7.8 Hz, 1H), 8.09 (dd, J=3.9, 8.3 Hz, 1 H), 8.26 ppm (d, J=7.8 Hz, 1 H); ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): $\delta = 27.20 \text{ ppm}$; IR (neat): $\tilde{\nu}_{max} = 1201 \text{ cm}^{-1}$ (P=O); HRMS(MALDI): m/z calcd for C30H28OPS: 467.1593; found: 467.1614 $[M+H^+].$

Compound 9: A mixture of compound 7 (44 mg, 0.12 mmol), 4-octyne (50 μ L, 0.35 mmol), Pd(OAc)₂ (8 mg, 0.04 mmol), K₂CO₃ (7 mg, 0.05 mmol), tetrabutylammonium bromide (24 mg, 0.074 mmol), and piv-

aloyl alcohol (16 µL, 0.14 mmol) in DMF (1.6 mL) was stirred for 3 d at 100–120 °C under an oxygen atmosphere. The mixture was then diluted with EtOAc/hexane (1:1) and insoluble substances were filtered off through a Celite bed. The aqueous layer was extracted with EtOAc/hexane (1:1) and the organic combines were washed with water, dried over MgSO₄, and evaporated. The residue was subjected to silica gel column chromatography (CH₂Cl₂/acetone = 10:1). The purple fluorescent fraction (R_f =0.33) was collected and evaporated to give compound **9** (29 mg, 51%) as an orange solid. M.p. 209–211°C (decomp); ¹H NMR (300 MHz, CD₂Cl₂): δ =1.25 (t, J=7.0 Hz, 3H), 1.27 (t, J=7.1 Hz, 3H), 1.81–1.91 (m, 4H), 3.20–3.25 (m, 2H), 3.33–3.38 (m, 2H), 3.96 (s, 3H), 7.24–7.37 (m, 5H), 7.43–7.49 (m, 2H), 7.59–7.70 (m, 4H), 8.04 (dd, J= 3.3, 8.0 Hz, 11H), 8.11 ppm (d, J=8.4 Hz, 11H); ³¹P['H] NMR (162 MHz, CDCl₃): δ =27.7 ppm; IR (neat): \tilde{v}_{max} =1196 cm⁻¹ (P=O); HRMS (ESI): m/z calcd for C₃₁H₃₁NOP: 464.2138: found: 464.2130 [M+H⁺].

X-ray crystallographic analyses: Single crystals of *cis*-**3**, **5**, and **6** were grown from CH₂Cl₂/hexane at room temperature. X-ray crystallographic measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo_{Ka} radiation (0.71070 Å) at -130 °C. The data were corrected for Lorentz and polarization effects. The structures were solved by using a direct method^[19] and refined by full-matrix least-squares techniques against F^2 by using SHELXL-97.^[20] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined py using the rigid model. All calculations were performed by using the Crystallographic software package^[21] except for the refinement. CCDC-894432 (*cis*-**3**), 894434 (**5**), and 894433 (**6**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: The structures of compounds **3–7** and the model compounds **8m** and **9m** were optimized by using DFT with the 6-31G* basis set.^[22] The functional of the DFT calculations was the Becke, three-parameter, Lee–Yang–Parr (B3LYP) exchange-correlation functional.^[23] We confirmed that the optimized geometries were not in saddle but in stable points. For compounds **5**, **6**, and **7**, the potential energy surfaces of the S₀ and S₁ states along the dihedral angles were performed by B3LYP and TD-B3LYP methods with the cc-pVDZ basis set to elucidate the relative stability and rotational barriers between two stable geometries.^[24] The effect of CH₂Cl₂ was estimated by the polarizable continuum model (PCM) method. The Cartesian coordinates are summarized in Table S1 in the Supporting Information. All calculations were carried out by using the Gaussian 09 suite of programs.^[25]

Fluorescence lifetime measurement and analysis: The time-resolved fluorescence spectra were measured by a streak camera (Hamamatsu Photonics, C4331). The output (780 nm, \approx 120 fs FWHM) of the optical parametric amplifier (Spectra Physics, TOPAS) excited by an amplified Ti:sapphire laser system (Spectra Physics, Spitfire XP, 800 nm, \approx 120 fs FWHM) was frequency-doubled to 390 nm by a BBO crystal, and used as an excitation pulse (for the excitation of compound 8, the excitation pulse of 360 nm was produced). The color sensitivity and the time-zero of the streak images were corrected as previously reported.^[26] Dichloromethane, acetonitrile, and benzene (spectroscopic grade) were used as received. As shown in Figure 7a, the spectral shape of compound 7 was dependent on the delay time after the excitation, suggesting that there are several species that show emission. In order to extract the number of species, which contributed to the time-resolved spectra, SVD analysis was applied to the time-resolved spectra.^[27] In the SVD analysis, the time-resolved spectra are decomposed into the spectral components and their time profiles weighted by their singular values (SVs). The spectral components that have large singular values are considered to be real components, and other components are disregarded as noise. The spectra components obtained by the SVD analysis for typical experimental conditions are given in Figure S2 in the Supporting Information. For example, the SV of the third component in Figure S2 in the Supporting Information is much smaller relative to the largest one (0.02) and could be neglected. All fluorescence spectra of compound 7 in different solvents were decomposed into two components spectra. Time profiles of the decomposed spectra are shown in Figure S2 in the Supporting Information.

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The largest one was simulated by a single exponential decay, whereas the smaller one was simulated by a double exponential. In order to obtain the correspondence between the SVD analysis and the real kinetics, we assumed the following rate equations [Eqs. (3) and (4)] for the excited state of 7 according to Figure 8.

$$\frac{d[CT_{A}^{*}]}{dt} = -(k_{AB} + k_{1})[CT_{A}^{*}] + k_{BA}[CT_{B}^{*}]$$
(3)

$$\frac{d[CT_B^*]}{dt} = -(k_{BA} + k_2)[CT_B^*] + k_{AB}[CT_A^*]$$
(4)

Under the assumption that k_{AB} and k_{BA} are faster than k_1 and k_2 , the concentration profiles of two excited states ($[CT_A^*]$ and $[CT_B^*]$) are given as shown in Equations (5) and (6),^[28] with k_{fast} and k_{slow} given by Equations (7) and (8), respectively.

$$[\mathrm{CT}^*_{\mathrm{A}}] = Ae^{-k_{\mathrm{fast}}t} + Be^{-k_{\mathrm{slow}}t}$$
⁽⁵⁾

$$[\mathrm{CT}^*_{\mathrm{B}}] = Ce^{-k_{\mathrm{fast}}t} + De^{-k_{\mathrm{slow}}t} \tag{6}$$

$$k_{\text{fast}} = k_{\text{AB}} + k_{\text{BA}} \tag{7}$$

$$k_{\text{slow}} = \frac{k_2 k_{\text{AB}} + k_1 k_{\text{BA}}}{k_{\text{AB}} + k_{\text{BA}}} \tag{8}$$

The pre-exponential factors A, B, C, and D are given as shown in Equations (9)–(12) in which $[CT_A*]_0$ and $[CT_B*]_0$ are the initial populations of the excited states of the A and B form, respectively.

$$A = \frac{[CT_{A}^{*}]_{0}k_{AB} - [CT_{B}^{*}]_{0}k_{BA}}{k_{AB} + k_{BA}}$$
(9)

$$B = \frac{([CT_{A}^{*}]_{0} + [CT_{B}^{*}]_{0})k_{BA}}{k_{AB} + k_{BA}}$$
(10)

$$C = \frac{-[CT_{A}^{*}]_{0}k_{AB} + [CT_{B}^{*}]_{0}k_{BA}}{k_{AB} + k_{BA}}$$
(11)

$$D = \frac{([CT_{A}^{*}]_{0} + [CT_{B}^{*}]_{0})k_{AB}}{k_{AB} + k_{BA}}$$
(12)

The SVD spectra are expressed by the linear combination of $[CT_A^*]$ and $[CT_B^*]$, and therefore it was concluded that the faster decay component obtained by the SVD time profile is ascribed to k_{fast} in Equation (1), and the slower one to k_{slow} in Equation (2). Because we could not determine the ratio of k_{AB} and k_{BA} and the initial concentration of each excited state, it was impossible to separate the apparent fluorescence spectra into two different components ascribed to CT_A^* and CT_B^* .

Acknowledgements

We thank Dr. Keiko Kuwata and Dr. Haruo Fujita (Kyoto University) for the measurements of the high-resolution mass spectra and the 2D NMR spectra, respectively. Y.H. and Y.M. also acknowledge Dr. Yuta Takano and Dr. Tomokazu Umeyama (Kyoto University) for their valuable comments on the photodynamics. This work was partially supported by Grants-in-Aid (No. 22350016) from MEXT, Japan.

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Received: August 28, 2012 Published online: November 9, 2012