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Effects of counter anions, *P*-substituents, and solvents on optical and photophysical properties of 2-phenylbenzo[*b*]phospholium salts⁺

Yoshinari Koyanagi,^a Shogo Kawaguchi,^b Kaori Fujii,^b Yoshifumi Kimura, ^b*^b Takahiro Sasamori, ^c Norihiro Tokitoh ^d and Yoshihiro Matano ^{*}

In this work, we investigated the effects of counter anions, P-substituents, and solvents on the optical and photophysical properties of 2-phenylbenzo[b]phospholium salts in solution. A series of 2-phenylbenzo[b] phospholium salts was prepared by P-alkylation or P-phenylation of 1,2-diphenylbenzo[b]phosphole followed by anion exchange reactions. X-ray crystallographic analyses of six benzo[b]phospholium salts showed that each phosphorus center has an onium nature with an essentially tetrahedral geometry. ¹H NMR and steady-state UV-vis absorption and fluorescence spectroscopic measurements of these phospholium salts revealed the pivotal role of counter-anion solvation. The observed results are discussed on the basis of the association-dissociation equilibrium between a contact ion pair (CIP) and a solventseparated ion pair (SSIP) in solution. The hexafluorophosphates exist as SSIPs and emit intense fluorescence, irrespective of the P-substituents and solvents. In contrast, the iodides are present as SSIPs in methanol but exist as equilibrium mixtures of the two emitting species, SSIP and CIP, in dichloromethane. As a consequence, fluorescence intensities of the iodides varied significantly depending on the solvents, P-substituents, and solution concentrations. These findings were studied in more detail using timeresolved fluorescence spectroscopy and fluorescence titration measurements. The light-emitting properties of the 2-phenylbenzo[b]phospholium halides in the CIPs rely on heavy atom effects derived from the counter halide anions on the S₁ state of the adjacent cationic benzo[b]phosphole π -systems. The present study suggests that 2-arylbenzo[b]phospholium salts would be promising scaffolds for developing new phosphole-based ionic fluorophores that are capable of responding to external stimuli such as anionic species and solvents.

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Introduction

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Recently, considerable effort has been focused on the development of phosphole-based π -electron systems (π -systems) for

^cGraduate School of Natural Sciences, Nagoya City University, Mizuho-ku, Nagoya 467-8501, Japan

their use in organic functional materials such as organic light-emitting diodes,¹ fluorescent imaging probes,² organic semiconductors³ and organic solar cells.⁴ In particular, 2-arylbenzo[b]phosphole π -systems have received considerable attention from both organic synthesis and materials chemistry fields because of their chemically tunable, stilbene-like π -frameworks bridged by a phosphorus atom.⁵ Several research groups have recently highlighted the substituent effects of 2-arylbenzo[b]phospholes on their fluorescence properties. For example, introducing an electron-donating amino group to the para position of 2-phenylbenzo[b]phosphole P-oxides provides charge-transfer character to the π -systems, resulting in enhanced ability to emit in the long-wavelength visible region.^{2,6} Substituents on the fused benzene ring of benzo[b]phosphole P-oxides also exert a significant influence on the π - π * transition energies and fluorescence intensities.⁷ In contrast to the P-oxides, little attention has been paid to the fluorescence properties of 2-arylbenzo[b]phospholium salts con-



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^aDepartment of Fundamental Sciences, Graduate School of Science and Technology, Niigata University, Nishi-ku, Niigata 950-2181, Japan

^bDepartment of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University, Kyotanabe 610-0321, Japan.

E-mail: yokimura@mail.doshisha.ac.jp

^dInstitute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

^eDepartment of Chemistry, Faculty of Science, Niigata University, Nishi-ku, Niigata 950-2181, Japan. E-mail: matano@chem.sc.niigata-u.ac.jp

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taining a phosphonio center in the π -framework.⁸ In 2015, Yamaguchi, Fukazawa, and co-workers reported that the fluorescence wavelength and intensity of **P1** were sensitive to solvent polarity.^{2*a*}

In recent years, Baumgartner and co-workers have reported phosphole lipids consisting of dithieno[3,2-b:2',3'-d]phospholium salts such as P2.9 These cationic fluorophores showed enhanced emission in the solid state and in solution, as a result of aggregation, and the unique photophysical behavior of the aggregates has been rationalized by considering conformation changes of their P-substituents. Ouite recently, we independently reported optical and photophysical properties of phosphonio-substituted fluorescent π -systems consisting of α, α' -linked thiophene-phosphole-thiophene skeleton P3.¹⁰ Notably, the fluorescence intensities of the iodide (X = I)varied widely depending on the solvents, whereas those of the hexafluorophosphate $(X = PF_6)$ were consistently high irrespective of the solvents. The observed results implied that an association-dissociation equilibrium between a solvent-separated ion pair (SSIP) and a contact ion pair (CIP) would play a crucial role in controlling the emission behavior of P3. It is well known that both internal and external heavy atom perturbations affect the rates of intersystem crossing processes between the singlet and triplet states. Thus, the iodide ions in the CIP of P3 (X = I) are likely to exert internal heavy atom effects on the excited-state dynamics of its π -system.¹¹ However, the intrinsic effects of counter anions, P-substituents, and solvents on the optical and photophysical properties of 2-arylbenzo[b]phospholium salts have not been studied comprehensively. A clear understanding of these effects is still an important subject in this field. Here, we report the first comprehensive study on the synthesis, structural, optical, and photophysical properties of a series of 2-phenylbenzo[b]phospholium salts (Fig. 1).

Results and discussion

Synthesis and characterization

2-Phenylbenzo[b]phospholium iodides 3, 5, and 7 were prepared by P-alkylation or Pd-catalyzed P-phenylation of 1,2diphenylbenzo[b]phosphole 2^{12} , which was obtained by the reduction of its *P*-oxide 1^{13} with trichlorosilane (Scheme 1). Anion exchange reactions of iodides 3, 5, and 7 with excess $NaPF_6$ gave the corresponding hexafluorophosphates 4, 6, and 8, respectively, whereas the reaction of 3 with excess NaCl vielded chloride 9. The P-(2-hydroxyethyl) (P-HE) derivatives 7 and 8 were slightly soluble in water. Compounds 3-9 were fully characterized using multinuclear (¹H, ¹³C, and ³¹P) NMR and IR spectroscopy and high-resolution mass spectrometry (HRMS). In the ${}^{31}P{}^{1}H{}$ NMR spectra of 3-9 in CD₂Cl₂ (ca. 10 mM), a singlet peak assignable to the cationic phosphorus center was observed at δ 28.5 to 35.2 ppm. The ³¹P{¹H} NMR spectra of 4, 6, and 8 displayed an additional septet peak due to the counter hexafluorophosphate ion at δ -144.4 to -144.5 ppm (${}^{1}J_{P-F}$ = 711 to 712 Hz). The HRMS spectra of 3-9 showed an intense peak derived from the fragmented phospholium ion $[M - X]^+$ (X = I, PF₆, Cl). The structures of 3–9 in the solid state and in solution will be discussed in the following sections on the basis of X-ray crystallography and ¹H NMR spectroscopy results.

Structures

Crystal structures of **3–8** were successfully characterized by X-ray crystallography (Fig. 2 and Table 1). As shown in Fig. 2, each phosphorus center has a distorted tetrahedral geometry with average C–P–C bond angles of $109.2–109.4^{\circ}$. The iodide and hexafluorophosphate ions are spatially separated from the



Fig. 1 Cationic phosphole-based π-systems.



Scheme 1 Synthesis of **3–9**. Inset: The numbering of hydrogen atoms (H_a , H_b and H_c).



Fig. 2 Crystal structures of (a) **3**, (b) **4**, (c) **5**, (d) **6**, (e) **7**, and (f) **8** (50% probability ellipsoids except for hydrogen atoms). Top (top) and side (bottom) views.

phosphorus center, indicating that **3–8** essentially have an onium nature. As summarized in Table 1, the C–C and C–P bond lengths in the phosphole ring (a–e) and the inter-ring bond length (f) of these six compounds are very close to each other. Thus, the *P*-substituents do not significantly alter the bond order in the 2-phenylbenzo[*b*]phosphole π -system. The inter-ring torsion angles (a–f–g in Table 1) of the *P*-phenyl derivatives (1,1,2-triphenylbenzo[*b*]phospholium salts) **5** (7.9°) and **6** (3.0°) are considerably small compared with those of the corresponding *P*-alkyl derivatives **3**, **4**, 7, and **8** (20.5–34.0°).

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Table 1 Selected bond parameters for 3-8

	$\begin{array}{c} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & &$								
	3	4	5	6	7	8			
Во	nd lengths ((Å)							
a	1.350(2)	1.349(3)	1.340(6)	1.352(2)	1.348(2)	1.349(2)			
b	1.466(2)	1.474(3)	1.477(6)	1.466(2)	1.467(2)	1.467(2)			
с	1.406(2)	1.397(3)	1.398(6)	1.398(2)	1.409(2)	1.403(2)			
d	1.785(2)	1.789(2)	1.795(4)	1.792(2)	1.785(1)	1.792(2)			
e	1.811(2)	1.801(2)	1.815(4)	1.810(1)	1.812(2)	1.807(2)			
f	1.472(2)	1.471(2)	1.473(6)	1.473(2)	1.470(2)	1.471(2)			
C -	P-C bond a	ngles (°)							
Ra	nge	0 ()							
	94.25(8)-	97.70(9)-	94.6(2)-	94.53(8)-	94.21(8)-	94.07(7)-			
	116.92(9)	113.8(1)	115.6(2)	114.52(7)	114.22(7)	113.22(8)			
Ave	erage								
	109.4	109.3	109.3	109.3	109.3	109.2			
Torsion angles (°): a–f–g									
	30.8	20.5	7.9	3.0	31.1	34.0			

The high planarity of the entire π -skeleton in 5 and 6 may be partly attributed to steric repulsion of the 2-phenyl group against the two *P*-phenyl groups. Within structure 3, the iodide ion is located close to the *peri*-hydrogen (H_a in Scheme 1), *ortho*-hydrogen (H_c) and one of the *P*-methyl hydrogen atoms, with inter-atomic distances of 2.96, 3.09, and 3.19 Å, respectively.¹⁴ Within structure 5, however, the iodide ion is located close to the other *peri*-hydrogen (H_b) with an inter-atomic distance of 2.90 Å. These distances are shorter than the sum of the van der Waals radii of hydrogen and iodine atoms (3.35 Å), indicating that the iodide ion in 3 and 5 weakly interacts with the above-mentioned hydrogens in the solid state.

In the structures of 7 and 8, the distances between the phosphorus and hydroxy oxygen atoms (2.97 Å for 7, 2.95 Å for 8) are shorter than the sum of their van der Waals radii (3.30 Å), reflecting intramolecular P...O coordination. Furthermore, the relatively short OH...I distance in 7 (2.68 Å) implies that there is a hydrogen-bonding interaction between the hydroxy group and the iodide ion.

To gain insight into the electrostatic interactions between the cation and anion of **3–9** in solution, we compared the ¹H NMR spectra of these compounds in two different solvents. Selected spectral features of **3–9** observed in CD_2Cl_2 (*ca.* 10 mM) are as follows. (i) **9** vs. **3** vs. **4** (Fig. 3a–c and Fig. S1a–c in the ESI†): the H_a, H_c (for the numbering, see Scheme 1), and H_{Me} protons of **3** and **9** are shifted largely downfield compared with the corresponding protons of **4**, whereas the other protons are shifted only slightly. The large downfield shifts of the specific protons around the phosphorus center indicate electrostatic interactions between the cationic phosphorus center and the counter halide anion in **3** and **9**. This interaction is more noticeable for **9** than for **3**, implying that the





Fig. 3 ¹H NMR spectra (δ = 9.0–7.2 ppm) of (a) 9, (b) 3, (c) 4, (d) 5, (e) 6, (f) 7, and (g) 8 in CD₂Cl₂ (*ca.* 10 mM).

phosphorus center interacts with the chloride ion more strongly than with the iodide ion. (ii) 5 vs. 6 (Fig. 3d and e): only the H_b proton of 5 is shifted largely downfield compared with the corresponding proton of 6, suggesting that the iodide ion in 5 is present close to H_b in CD₂Cl₂. Two phenyl groups on the phosphorus atom in 5 may sterically hinder access of the iodide ion to the phosphorus center, as deduced from the crystal structure of 5 (Fig. 2c). The regiospecific downfield shift of the H_b proton also suggests the existence of anion- π or anion-(H-C) interactions between the iodide ion and the positively charged benzo[b]phosphole π -framework. (iii) 7 vs. 8 (Fig. 3f, g and Fig. S1d, e in the ESI[†]): two characteristic features should be noted. First, the H_a and H_c protons of 7 appeared further downfield than the corresponding protons of 8. The iodide ion in 7 may be located close to the phosphorus center, similar to the case of 3. Second, the hydroxy proton of 7 is shifted about 2 ppm further downfield than that of 8. It is likely that a hydrogen-bonding interaction between the iodide ion and the hydroxy group in 7 is present even in CD_2Cl_2 . The spectral features of 3-9 in CD₃OD (Fig. S2, S16, and S18 in the ESI[†]) are quite different from those in CD₂Cl₂; when the P-substituents are the same, there is almost no difference in the spectral features among iodides (3, 5, 7), hexafluorophosphates (4, 6, 8), and chloride (9). These data suggest that the 2-phenylbenzo[b]phospholium salts exist as SSIPs in CD_3OD_3 irrespective of the counter anions.

Optical and photophysical properties

To reveal the effects of counter anions and P-substituents on the optical properties of the 2-phenylbenzo[b]phospholium salts, we measured steady-state UV-vis absorption and fluorescence spectra of 3-9 in solution (Table 2 and Fig. 4). As listed in Table 2, the absorption and emission maxima of 3-9 in CH₂Cl₂ are λ_{abs} = 354–362 nm and λ_{em} = 446–453 nm, respectively, whereas those in MeOH are $\lambda_{abs} = 353-360$ nm and $\lambda_{em} = 440-453$ nm, respectively. Stokes shifts of 3-9 $(5510-5820 \text{ cm}^{-1})$ are larger than that of *P*-oxide 1 (4930 \text{ cm}^{-1}) in CH_2Cl_2).^{6c} The influence of the counter anions on the λ_{abs} and λ_{em} values is negligible or very small for all the 2-phenylbenzo[b]phosphole π -systems; *i.e.*, the π - π * transition energies and spectral shapes of 3, 5, and 7 are almost identical to those of 4, 6, and 8, respectively. The absorption and emission bands of 5 and 6 are slightly red-shifted compared with the corresponding bands of 3 and 4; the optical HOMO-LUMO gaps of 5 and 6 (ΔE_{op} = 3.05–3.06 eV) are narrower than those of 3 and 4 ($\Delta E_{\rm op}$ = 3.09–3.13 eV). This may reflect the difference in planarity of their π -frameworks; *i.e.*, the 2-phenyl group in 5/6 is less twisted against the phosphole ring than that in 3/4 (Fig. 2a–d). The solvent dependence of the ΔE_{op} values of 5/6 ($\Delta \Delta E_{op} = 0.01 \text{ eV}$) is small, implying that the conformational change of the π -framework in 5/6 is little affected by the solvents. There are small differences in reduction potentials (E_{red}) of 4, 6, and 8 (ΔE_{red} = 0.05–0.08 V), indicating that the LUMO energy levels of the present π -systems are slightly affected by the P-substituents (Table 2 and Fig. S3 in the ESI[†]).

To investigate the effects of counter anions, *P*-substituents, and solvents on the fluorescence properties of the present 2-phenylbenzo[*b*]phospholium salts, we measured the concen-

Table 2 Optical and electrochemical data for 3–9

Compd	Solvent	$\lambda_{\rm abs} (\log \varepsilon)^a$	$\lambda_{\rm em}{}^b$	$\Delta E_{\mathrm{op}}{}^{c}$	Stokes shift ^d
3	CH_2Cl_2	358 (3.99)	447	3.09	5560
4^{e}	CH_2Cl_2	358 (4.03)	446	3.09	5510
5	CH_2Cl_2	362 (3.88)	453	3.05	5550
6 ^e	CH_2Cl_2	362 (3.90)	453	3.05	5550
7	CH_2Cl_2	357 (3.92)	450	3.09	5790
8 ^e	CH_2Cl_2	356 (3.94)	449	3.09	5820
9	CH_2Cl_2	354 (3.91)	447	3.10	5640
3	MeOH	354 (n.d.)	442	3.13	5620
4	MeOH	354 (n.d.)	442	3.13	5620
5	MeOH	359 (n.d.)	452	3.06	5730
6	MeOH	360 (n.d.)	453	3.06	5700
7	MeOH	354 (n.d.)	445	3.12	5780
8	MeOH	353 (n.d.)	444	3.12	5810
9	MeOH	354 (n.d.)	440	3.13	5520
7	H_2O	354 (n.d.)	445	3.12	5780
8	H_2O	354 (n.d.)	444	3.12	5730

^{*a*} Absorption maximum (in nm). Values in parenthesis are molar extinction coefficients at λ_{abs} . n.d. = not determined. ^{*b*} Fluorescence maximum (in nm) excited at λ_{abs} . ^{*c*} Optical HOMO–LUMO gap (in eV) determined from the intersection of the normalized absorption and emission spectra. ^{*d*} $\Delta \nu = 1/\lambda_{abs} - 1/\lambda_{em}$ (in cm⁻¹). ^{*e*} Reduction potentials (E_{red}) were measured in CH₂Cl₂ with Bu₄NPF₆ as the supporting electrolyte. $E_{red} = -1.57$ (4), -1.52 (6), and -1.60 V (8) vs. ferrocene/ferrocenium couple (Fc/Fc⁺). All redox processes were irreversible.



Fig. 4 UV-vis absorption (solid lines) and fluorescence (dotted lines) spectra of (a) 3, 4, (b) 5, 6, and (c) 7, 8 in CH₂Cl₂. Excitation wavelength $(\lambda_{ex}) = \lambda_{abs}$. Concentration dependence of fluorescence intensities of (d) 3, 4, (e) 5, 6, and (f) 7, 8 in CH₂Cl₂. $\lambda_{ex} = \lambda_{abs}$.

tration dependence of the fluorescence intensities of **3–8** in CH₂Cl₂. As shown in Fig. 4d–f, iodides **3**, **5**, and **7** exhibited clear concentration quenching of fluorescence in the range of Abs = 0.1–0.5 (at λ_{ex}), whereas hexafluorophosphates **4**, **6**, and **8** showed only small concentration quenching. The fluorescence intensities of **3**, **5**, and **7** are appreciably lower than those of **4**, **6**, and **8** at any concentrations. The *P*-substituents also have definite impacts on the quenching behavior; the degree of fluorescence quenching is in the order **5** < **3** < **7**. These results will be discussed later.

For deeper insights into the photophysical properties of **3–8**, we next measured fluorescence quantum yields (Φ_f) and fluorescence lifetimes (τ_f) of these compounds (Table 3). The radiative and non-radiative decay rate constants (k_r and k_{nr} , respectively) determined from the Φ_f and τ_f values are also listed in Table 3. The results are summarized as follows. (1) The Φ_f values vary from 0.36 to 0.89 depending on the *P*-substituents and solvents. (2) The Φ_f values of **4**, **6**, and **8** in CH₂Cl₂ are larger than those in MeOH, whereas the Φ_f values of **3**, **5**, and 7 in CH₂Cl₂ are smaller than those in MeOH. (3) In MeOH, the Φ_f and τ_f values of **3**, **5**, and 7 are the same as or close to those of **4**, **6**, and **8**, respectively. In CH₂Cl₂, the Φ_f values of the iodides are smaller than those of the hexafluorophosphates, as deduced from Fig. 4d–f. (4) The fluorescence decay curves of **3–8** obeyed first-order kinetics, except for two

Compd	Solvent	Abs ^a	${\Phi_{\mathrm{f}}}^{b}$	${\tau_{\mathrm{f}}}^{c}/\mathrm{ns}$	$k_{\rm r}^{\ d}/{\rm s}^{-1}$	$k_{\rm nr}{}^d/{\rm s}^{-1}$
3	CH_2Cl_2	0.1	0.57	$7.7 (0.96)^{e}$ 1 9 (0.04) ^e	$7.7 \times 10^{7 f}$	5.7×10^{7f}
4	CH ₂ Cl ₂	0.1	0.75	8.2 ^g	9.1×10^{7}	$3.0 imes 10^7$
5	CH_2Cl_2	0.1	0.80	8.5	$9.4 imes 10^7$	$2.4 imes 10^7$
6	CH_2Cl_2	0.1	0.87	9.3 ^g	$9.4 imes 10^7$	$1.4 imes 10^7$
7	CH_2Cl_2	0.1	0.36	$7.5 (0.90)^{e,g}$	$5.2 \times 10^{7} f$	$8.1 \times 10^{7} f$
				$1.4(0.10)^{e,g}$		
8	CH_2Cl_2	0.1	0.89	7.8	$1.1 imes 10^8$	$1.4 imes 10^7$
3	MeOH	0.1	0.65	7.9	$8.2 imes 10^7$	$4.4 imes 10^7$
4	MeOH	0.1	0.65	8.3^{h}	$7.8 imes 10^7$	4.2×10^7
5	MeOH	0.1	0.81	9.1	$8.9 imes 10^7$	$2.1 imes 10^7$
6	MeOH	0.1	0.76	9.8^{i}	7.8×10^{7}	$2.4 imes 10^7$
7	MeOH	0.2	0.68	8.4	$8.1 imes 10^7$	3.8×10^{7}
8	MeOH	0.2	0.68	8.4	$8.1 imes 10^7$	3.8×10^{7}
7	H_2O	0.2	0.82	10.0	$8.2 imes 10^7$	$1.8 imes 10^7$
0	ч о	0.2	0.83	10.2	8.1×10^{7}	1.7×10^{7}

^{*a*} Absorbance at λ_{abs} . ^{*b*} Fluorescence quantum yield. $\lambda_{ex} = \lambda_{abs}$. ^{*c*} Fluorescence lifetime. ^{*d*} Radiative and nonradiative decay rate constants (k_r and k_{nr} , respectively) determined from the Φ_f and τ_f values. ^{*e*} Values in parentheses are the relative amplitudes of each component. ^{*f*} Radiative and nonradiative decay rate constants determined by the averaged lifetime weighted by the amplitude. ^{*g*} Abs = 0.12. ^{*h*} Abs = 0.17. ^{*i*} Abs = 0.15.

cases (3 and 7 in CH₂Cl₂). The fluorescence decay profiles of 3 and 7 in CH₂Cl₂ were fit with a double exponential function with a small contribution of the faster decay component. Thus, two emitting species with different $\tau_{\rm f}$ values exist in CH₂Cl₂. (5) Changing the solvent from CH₂Cl₂ to MeOH slightly decreased the $k_{\rm r}$ values, but increased the $k_{\rm nr}$ values of **4**, **6**, and **8**. (6) The *P*-methyl and *P*-phenyl groups have different effects on the non-radiative pathways from the S₁ state; the $k_{\rm r}$ values of **4** are almost the same as those of **6**, whereas the $k_{\rm nr}$ values of **4** are about twice as much as those of **6**. The observed results (1)–(6) can be rationalized by considering an association–dissociation equilibrium between two emitting species, CIP and SSIP, in solution (eqn (1)):



Obviously, the fluorescence properties of 3–8 reflect the varying degrees of electrostatic interactions between the benzo [b]phosphole cation and counter anions. In the polar protic solvent, MeOH (dielectric constant = 33), the counter anion should be fully solvated through hydrogen-bonding and dipole interactions, resulting predominantly in SSIP formation. This explains well the first-order kinetics observed for 3–8 in MeOH; the emitting species correspond to the solvent-separated benzo[b]phosphole cations in the S₁ state. This is also inferred from the fact that the counter anions have no influence on the $\Phi_{\rm f}$ and $\tau_{\rm f}$ values in MeOH. In the less-polar, aprotic solvent, CH₂Cl₂ (dielectric constant = 9), the CIP/SSIP ratio should vary depending on the counter anions as well as the solution concentration. In the cases of 4, 6, and 8 in

CH₂Cl₂, the SSIP should be the major species because the non-nucleophilic hexafluorophosphate ion cannot access the cationic phosphorus center. Indeed, the fluorescence decay curves of these compounds obeyed first-order kinetics. The relatively large $\Phi_{\rm f}$ values of **4**, **6**, and **8** in CH₂Cl₂ compared with those in MeOH indicate the intrinsic difference in the solvation effects between CH₂Cl₂ and MeOH on the excited-state of the 2-phenylbenzo[*b*]phospholium π -systems.

In the cases of 3, 5, and 7 in CH₂Cl₂, both the CIP and SSIP should be present at equilibrium, and the $\tau_{\rm f}$ and $\Phi_{\rm f}$ values would be influenced by interaction with the counter iodide ion. This intrinsically nucleophilic anion exerts the heavy atom effects on the S_1 states of the adjacent cationic π -systems, resulting in acceleration of the intersystem crossing processes. Thus, the static quenching of the S_1 state of the cationic π -systems would be more pronounced in CIPs than in SSIPs. The shorter and longer lifetime components observed for the iodides (3 and 7) in CH₂Cl₂ probably correspond to CIPs and SSIPs, respectively. This interpretation is supported by the observation that the longer $\tau_{\rm f}$ values obtained for 3 (7.7 ns) and 7 (7.5 ns) are comparable to the $\tau_{\rm f}$ values observed for 4 (8.2 ns) and 8 (7.8 ns). For the iodides in CH_2Cl_2 , increasing the concentration shifts the equilibrium position from the SSIP to CIP, leading to fluorescence quenching, as shown in Fig. 4d-f. Among the three iodides, the 2-HE derivative 7 exhibited the largest quenching in CH2Cl2, in which the OH…I hydrogen-bonding interaction may contribute to shift the equilibrium to the CIP side and to strengthen the heavy atom effects of the iodide ion in the CIP. The photophysical behavior of 5 is somewhat complicated. The fluorescence decay of 5 in CH_2Cl_2 obeyed first-order kinetics with a τ_f value of 8.5 ns, indicating that the SSIP is the predominant species at the concentration of the measurement (15 µM). At higher concentrations, however, the equilibrium is probably shifted to the CIP side, as deduced from Fig. 4e. It should be noted that the $k_{\rm nr}$ values observed for 3/4 (4.2–4.4 \times $10^7~{\rm s}^{-1}$ in MeOH) are about twice as much as those observed for 5/6 (2.1–2.4 × 10^7 s^{-1} in MeOH). Although these particular substituent effects are not clearly understood yet, the distorted π -framework in 3/4 (Fig. 2a and b) might undergo conformational relaxation from the S_1 state more rapidly than does the planar π -framework in 5/6 (Fig. 2c and d).

Fluorescence titration measurements

To evaluate the validity of the above interpretation, as well as to compare the effects of counter halide ions on the fluorescence properties of a 2-phenylbenzo[*b*]phospholium ion, we performed fluorescence titration measurements on **4** in CH_2Cl_2 with a tetrabutylammonium halide (Bu₄NX; X = Cl, I) additive. As shown in Fig. 5 and Fig. S4a in the ESI,† the fluorescence of **4** was gradually quenched by increasing the amount of Bu₄NX; at the high concentrations, the fluorescence intensities were in the order (X =) Cl > I. These results probably reflect the difference in the heavy atom effects of the respective counter halide ions in the CIPs; the heavier iodine atom exerts a greater heavy atom effect on the cationic π -system. A similar



Fig. 5 Fluorescence titration measurements of 4 (25 μ M) with Bu₄NX (X = Cl, I) in CH₂Cl₂ at 25 °C. λ_{ex} = 358 nm (λ_{abs}). Changes in the fluorescence spectra (a, b) and fluorescence intensities (c) by the addition of Bu₄NX.

spectral change was observed in a fluorescence titration experiment of 3 with Bu₄NCl (Fig. S4b in the ESI[†]). The $\lambda_{abs}/\lambda_{em}$ and $\Phi_{\rm f}$ values of $[3 + Bu_4NCl (excess)]$ are almost identical to those of $[4 + Bu_4NCl (excess)] (\lambda_{abs}/\lambda_{em} = 355/442 \text{ nm}, \Phi_f = 0.14-0.15),$ indicating that anion exchange reactions of 3/4 with Bu₄NCl took place to form the same CIP of chloride 9 as the major species. The conversion from 3 to 9 by the addition of Bu₄NCl was confirmed by ¹H NMR spectroscopy (Fig. S5 in the ESI[†]). Furthermore, we measured the concentration dependence of the halide ion on the decay curves of 4 and 9 in CH_2Cl_2 (Fig. S6 in the ESI[†]). At higher halide concentrations, the amplitude of the faster component (CIP) increased relative to the slower component (SSIP). This result suggests that the change in the ratio of these two emitting species contributes to the decay kinetics of the fluorescent 2-phenylbenzo[b]phospholium ion.‡

Reaction of 7 in alkaline solution

Compounds 7 and 8 are slightly soluble in H₂O, and the resulting aqueous solutions are highly fluorescent ($\Phi_f = 0.82-0.83$). Considering possible application to a water-soluble fluorescent probe, we examined the chemical stability of 7 in aqueous media. Compound 7 was stable in neutral H₂O–MeOH (1:1) solution but decomposed in the presence of K₂CO₃ (*ca.* 0.08

 $[\]ddagger$ The spectral shapes of the normalized absorption and emission spectra of **3–8** in CH₂Cl₂ did not change in the range of Abs = 0.1–0.5. In addition, the timeresolved fluorescence spectroscopy of **3** in CH₂Cl₂ did not show any transient emissive species that would be assignable to an excimer or exciplex in the range of Abs = 0.1–1. Therefore, we can rule out the other possible concentrationquenching mechanisms caused by the chromophore–chromophore interaction in the ground/excited states.

M) to give 2-phosphorylstilbene **10** as the main product (eqn (2)). Thin-layer chromatography and ¹H NMR spectroscopy showed that conversion from 7 to **10** proceeded cleanly and quantitatively, while the isolated yield of **10** was 27% because of concomitant loss during the chromatographic purification process. Although the instability of 7 prevents its use as a water-soluble fluorescent probe, quantitative conversion from 7 to **10** in alkaline media would give valuable information about the molecular design of chemically stable benzo[*b*] phosphole-based ionic fluorescent materials.



Conclusions

We prepared seven kinds of 2-phenylbenzo[b]phospholium salts to comprehensively study the effects of counter anions, *P*-substituents, and solvents on the optical and photophysical properties of cationic 2-phenylbenzo[b]phosphole π -systems. The target compounds were prepared by P-alkylation or *P*-phenylation of 1,2-diphenylbenzo[*b*]phosphole followed by anion exchange reactions and characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography. The hexafluorophosphates are highly fluorescent, irrespective of the P-substituents and solvents. In contrast, the iodides are basically present in equilibrium between the solvent-separated ion pair and contact ion pair, and their emission properties vary considerably depending on the solvents, P-substituents, solution concentrations, and amount of halide additives. Steady-state and time-resolved fluorescence spectroscopy of these emissive 2-phenylbenzo[b]phospholium salts revealed that internal heavy atom effects of the counter halide ions play a pivotal role in controlling the fluorescence properties of adjacent cationic benzo[b]phosphole π -systems in contact ion pairs. Furthermore, the P-substituents have a definite impact on the structures and excited-state dynamics of these cationic π -frameworks. The present findings suggest that 2-arylbenzo[b] phospholium salts would be promising scaffolds for the development of new phosphole-based ionic fluorophores that are capable of responding to external stimuli such as anionic species and solvents.

Experimental

General

All melting points were recorded on Yazawa micro melting point apparatus and are uncorrected. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian 400 MHz or 700 MHz spectrometer or a Bruker NanoBay 400 MHz spectrometer.

Chemical shifts are reported in ppm as relative values vs. tetramethylsilane (for ¹H and ¹³C) or phosphoric acid (for ³¹P). High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer. UV-vis absorption and fluorescence spectra were measured at room temperature on JASCO V-530 and EP-8300 spectrometers, respectively. All the excitation spectra were essentially identical to the corresponding absorption spectra. Absolute fluorescence quantum yields were measured on a Hamamatsu Photonics Quantaurus-QY spectrometer. Redox potentials were measured on a CH Instruments model 650E electrochemical workstation using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ [0.01 M AgNO₃, 0.1 M Bu₄NPF₆ (MeCN)] reference electrode. The potentials were calibrated with ferrocene/ferrocenium (Fc/Fc⁺). Compounds 1 and 2 were prepared according to the reported procedure.^{6c,15} Other chemicals and solvents were of reagent grade quality and used without further purification. Thin-layer chromatography was performed with Alt. 5554 DC-Alufolien Kieselgel 60 F254 (Merck), and preparative column chromatography was performed using silica gel (spherical, neutrality). All reactions were performed under an argon or a nitrogen atmosphere.

Synthesis and characterization

3. To a solution of 2 (0.197 g, 0.69 mmol) in CH₂Cl₂ (10 mL) was added iodomethane (0.65 mL, 10 mmol), and the reaction mixture was stirred for 48 h at room temperature. The resulting mixture was evaporated under reduced pressure to obtain a solid residue, which was recrystallized from CH₂Cl₂/hexane to give 3 as a pale yellow solid (0.277 g, 94%): $R_f = 0.3$ (CH₂Cl₂/ MeOH = 10/1; mp 268–270 °C; ¹H NMR (400 MHz, CD₂Cl₂, 11 mM): δ = 3.09 (d, J_{H-P} = 14.4 Hz, 3H), 7.44–7.48 (m, 5H), 7.59-7.64 (m, 1H), 7.66-7.72 (m, 2H), 7.78-7.85 (m, 3H), 8.09–8.15 (m, 2H), 8.17 (d, J_{H-P} = 36.8 Hz, 1H), 8.47–8.52 (m, 1H) ppm, ¹H NMR (400 MHz, CD₃OD, 10 mM): δ = 2.93 $(d, J_{H-P} = 15.2 \text{ Hz}, 3H), 7.42-7.48 \text{ (m, 3H)}, 7.55-7.60 \text{ (m, 2H)},$ 7.62-7.67 (m, 1H), 7.68-7.73 (m, 2H), 7.83-7.97 (m, 5H), 8.01–8.06 (m, 1H), 8.40 (d, J_{H-P} = 37.2 Hz, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 8.3 (d, J_{C-P} = 49.4 Hz), 115.8 (d, J_{C-P} = 82.7 Hz), 123.8 (d, J_{C-P} = 94.1 Hz), 126.6 (d, J_{C-P} = 6.8 Hz), 127.0 (d, J_{C-P} = 9.1, Hz), 129.5 (d, J_{C-P} = 11.4 Hz), 129.6 (d, J_{C-P} = 78.9 Hz), 130.0 (s), 130.7 (s), 130.8 (d, J_{C-P} = 13.7 Hz), 131.2 (d, J_{C-P} = 12.2 Hz), 133.0 (d, J_{C-P} = 11.4 Hz), 133.5 (d, J_{C-P} = 12.1 Hz), 135.7 (d, J_{C-P} = 3.0 Hz), 135.9 (d, J_{C-P} = 2.2 Hz), 143.2 (d, J_{C-P} = 25.0 Hz), 144.0 (d, J_{C-P} = 16.7 Hz) ppm; ${}^{31}P{}^{1}H$ NMR (162 MHz, CD₂Cl₂, 10 mM): δ = 31.0 ppm; ³¹P{¹H} NMR (162 MHz, CD₃OD, 10 mM): δ = 31.4 ppm; HRMS (ESI): $m/z = 301.1132 ([M - I]^+, calcd 301.1141).$ §

4. A mixture of 3 (49 mg, 0.11 mmol), NaPF₆ (0.387 g, 2.3 mmol), CH_2Cl_2 (2.5 mL), and MeCN (1 mL) was stirred at room temperature. After 1 h, the mixture was washed with

[§]Although we could not obtain sufficient elemental analysis results because of contamination of aerobic moisture and/or recrystallization solvents, the purity of the obtained compounds could be confirmed by spectroscopic analyses.

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water (2.5 mL). NaPF₆ (0.387 g, 2.3 mmol) was then added, and the resulting mixture was stirred for 2 h. After addition of CH₂Cl₂ (10 mL), the mixture was washed with water $(3 \times 10 \text{ mL})$, dried over Na₂SO₄, and evaporated to obtain a solid residue, which was then chromatographed on silica gel using CH₂Cl₂/MeOH (20/1) as an eluent. Compound 4 was isolated as a colorless solid (41 mg, 81%) by recrystallization from CH_2Cl_2 /hexane: $R_f = 0.4$ (CH_2Cl_2 /MeOH = 10/1); mp 79–81 °C; IR (KBr): $\nu_{\text{max}} = 837$ (P–F) cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 10 mM): δ = 2.67 (d, J_{H-P} = 14.0 Hz, 3H), 7.40–7.48 (m, 5H), 7.60-7.66 (m, 1H), 7.68-7.73 (m, 2H), 7.79-7.91 (m, 6H), 8.10 (d, J_{H-P} = 37.6 Hz, 1H) ppm, ¹H NMR (400 MHz, CD₃OD, 9 mM): δ = 2.91 (d, J_{H-P} = 14.8 Hz, 3H), 7.41–7.47 (m, 3H), 7.55-7.60 (m, 2H), 7.61-7.67 (m, 1H), 7.68-7.73 (m, 2H), 7.83–7.96 (m, 5H), 7.99–8.04 (m, 1H), 8.39 (d, J_{H-P} = 37.6 Hz, 1H) ppm; ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ = 5.2 (d, J_{C-P} = 50.8 Hz), 115.6 (d, J_{C-P} = 81.9 Hz), 123.4 (d, J_{C-P} = 94.1 Hz), 126.5 (d, J_{C-P} = 6.8 Hz), 127.4 (d, J_{C-P} = 9.1, Hz), 129.4 (d, J_{C-P} = 11.4 Hz), 129.6 (d, J_{C-P} = 78.9 Hz), 129.9 (s), 130.6 (s), 131.0 (d, J_{C-P} = 13.6 Hz), 131.0 (d, J_{C-P} = 11.4 Hz), 131.1 (d, J_{C-P} = 11.3 Hz), 131.9 (d, J_{C-P} = 12.1 Hz), 135.9 (d, J_{C-P} = 3.1 Hz), 136.2 (d, $J_{C-P} = 1.5 \text{ Hz}$, 143.7 (d, $J_{C-P} = 25.0 \text{ Hz}$), 144.5 (d, $J_{C-P} = 16.7 \text{ Hz}$) ppm; ${}^{31}P{}^{1}H$ NMR (162 MHz, CD₂Cl₂, 10 mM): $\delta = -144.4$ (septet, $J_{P-F} = 712$ Hz), 29.8 ppm; ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CD₃OD, 10 mM): δ = -144.6 (septet, J_{P-F} = 708 Hz), 31.4 ppm; HRMS (ESI): m/z = 301.1133 ([M – PF₆]⁺, calcd 301.1141).

5. To a solution of 2 (0.275 g, 0.96 mmol) in xylene (5 mL) was added iodobenzene (220 µL, 2.0 mmol) and Pd₂(dba)₃ (47 mg, 0.051 mmol), and the reaction mixture was refluxed for 3 h. The resulting suspension was cooled to room temperature, and the precipitate was filtered, washed with hexane, and dissolved in CH₂Cl₂. The resulting solution was evaporated under reduced pressure to obtain a solid residue, which was recrystallized from CH₂Cl₂/hexane to give 5 as a yellow solid (0.381 g, 81%): $R_f = 0.3 (CH_2Cl_2/MeOH = 10/1)$; mp 230–232 °C; ¹H NMR (400 MHz, CD_2Cl_2 , 10 mM): $\delta = 7.41-7.54$ (m, 5H), 7.66-7.76 (m, 5H), 7.81-7.93 (m, 7H), 7.94-7.99 (m, 1H), 8.00–8.03 (m, 1H), 8.46 (d, J_{H-P} = 38.4 Hz, 1H) ppm; ¹H NMR (400 MHz, CD₃OD, 10 mM): δ = 7.41–7.48 (m, 3H), 7.56–7.61 (m, 2H), 7.67-7.72 (m, 1H), 7.73-7.79 (m, 4H), 7.90-8.00 (m, 8H), 8.10–8.15 (m, 1H), 8.51 (d, J_{H-P} = 38.4 Hz, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 114.7 (d, J_{C-P} = 83.4 Hz), 123.2 (d, J_{C-P} = 96.3 Hz), 126.9 (d, J_{C-P} = 6.9 Hz), 128.5 (d, J_{C-P} = 78.9, Hz), 128.6 (d, J_{C-P} = 9.1 Hz), 129.7 (s), 130.0 (d, J_{C-P} = 11.4 Hz), 130.5 (s), 131.1 (d, J_{C-P} = 13.6 Hz), 131.3 (d, $J_{\rm C-P}$ = 11.4 Hz), 131.4 (d, $J_{\rm C-P}$ = 10.7 Hz), 133.5 (d, $J_{\rm C-P}$ = 11.4 Hz), 136.2 (d, *J*_{C-P} = 3.1 Hz), 136.3 (d, *J*_{C-P} = 2.3 Hz), 144.0 $(d, J_{C-P} = 25.0 \text{ Hz}), 146.6 (d, J_{C-P} = 16.7 \text{ Hz}) \text{ ppm}; {}^{31}\text{P}{}^{1}\text{H} \text{NMR}$ (162 MHz, CD_2Cl_2 , 10 mM): δ = 28.5 ppm; ³¹P{¹H} NMR (162 MHz, CD₃OD, 10 mM): δ = 28.9 ppm; HRMS (ESI): m/z = $363.1290 ([M - I]^+, calcd 363.1297).$

6. According to a similar procedure described for the synthesis of 4, 6 was prepared from 5. Compound 6 was isolated as a pale yellow solid in 71% yield based on 5: $R_{\rm f}$ = 0.5 (CH₂Cl₂/MeOH = 10/1); mp 218–220 °C; IR (KBr): $\nu_{\rm max}$ = 836 (P–F) cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 10 mM): δ = 7.41–7.50

(m, 5H), 7.65–7.75 (m, 5H), 7.77–7.93 (m, 9H), 8.10 (d, J =0.4 Hz, J_{H-P} = 38.0 Hz, 1H) ppm; ¹H NMR (400 MHz, CD₃OD, 10 mM): δ = 7.41–7.48 (m, 3H), 7.56–7.61 (m, 2H), 7.66–7.72 (m, 1H), 7.73-7.78 (m, 4H), 7.90-7.99 (m, 8H), 8.09-8.14 (m, 1H), 8.49 (d, J_{H-P} = 38.4 Hz, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl_3 : δ = 114.8 (d, $J_{\text{C-P}}$ = 83.5 Hz), 123.3 (d, $J_{\text{C-P}}$ = 95.6 Hz), 126.9 (d, J_{C-P} = 6.9 Hz), 128.2 (d, J_{C-P} = 9.1, Hz), 129.3 (d, J_{C-P} = 79.7 Hz), 129.9 (s), 130.1 (d, J_{C-P} = 10.6 Hz), 130.7 (s), 131.2 (d, $J_{\rm C-P}$ = 13.7 Hz), 131.3 (d, $J_{\rm C-P}$ = 10.7 Hz), 131.5 (d, $J_{\rm C-P}$ = 11.4 Hz), 133.5 (d, J_{C-P} = 11.3 Hz), 136.3 (d, J_{C-P} = 3.1 Hz), 136.5 (d, J_{C-P} = 2.3 Hz), 144.0 (d, J_{C-P} = 25.0 Hz), 146.1 (d, $J_{C-P} = 16.7 \text{ Hz}$ ppm; ${}^{31}P{}^{1}H$ NMR (162 MHz, CD_2Cl_2 , 10 mM): $\delta = -144.5$ (septet, $J_{P-F} = 711$ Hz), 28.6 ppm; ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CD₃OD, 10 mM): $\delta = -144.6$ (septet, $J_{P-F} = 708$ Hz), 29.0 ppm; HRMS (ESI): m/z = 363.1290 ([M - PF₆]⁺, calcd 363.1297).

7. To a solution of 2 (0.226 g, 0.79 mmol) in toluene (10 mL) was added 2-iodoethanol (0.20 mL, 2.6 mmol), and the reaction mixture was refluxed for 15 h. The resulting mixture was evaporated under reduced pressure to obtain a solid residue, which was recrystallized from CH2Cl2/hexane to give 7 as a pale yellow solid (0.329 g, 91%): $R_{\rm f} = 0.2 (CH_2Cl_2/$ MeOH = 10/1; mp 174–176 °C; ¹H NMR (400 MHz, CD₂Cl₂, 10 mM): δ = 2.97–3.06 (m, 1H), 3.83–3.92 (m, 1H), 4.10–4.20 (m, 1H), 4.25-4.37 (m, 1H), 4.83 (s, 1H), 7.40-7.46 (m, 5H), 7.60–7.67 (m, 3H), 7.75–7.83 (m, 3H), 8.01 (d, J_{H-P} = 35.6 Hz, 1H), 8.02–8.08 (m, 1H), 8.27–8.31 (m, 1H) ppm; ¹H NMR (400 MHz, CD_3OD): $\delta = 3.36-3.46$ (m, 1H), 3.84-4.06 (m, 3H), 7.42-7.47 (m, 3H), 7.55-7.60 (m, 2H), 7.62-7.70 (m, 3H), 7.79-7.90 (m, 3H), 7.91-7.98 (m, 2H), 8.07-8.12 (m, 1H), 8.32 (d, J = 0.6 Hz, $J_{H-P} = 36.6$ Hz, 1H) ppm; ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ = 25.4 (d, J_{C-P} = 46.2 Hz), 55.6 (d, J_{C-P} = 6.9 Hz), 116.6 (d, J_{C-P} = 81.2 Hz), 122.3 (d, J_{C-P} = 92.6 Hz), 126.6 (d, J_{C-P} = 6.1 Hz), 126.8 (d, J_{C-P} = 9.1, Hz), 129.7 (d, J_{C-P} = 10.6 Hz), 129.9 (s), 130.7 (s), 130.7 (d, *J*_{C-P} = 12.9 Hz), 131.0 (d, J_{C-P} = 12.1 Hz), 131.2 (d, J_{C-P} = 76.6 Hz), 132.9 (d, J_{C-P} = 11.4 Hz), 133.9 (d, J_{C-P} = 11.4 Hz), 135.4 (d, J_{C-P} = 3.1 Hz), 135.8 (d, $J_{C-P} = 2.3 \text{ Hz}$, 142.8 (d, $J_{C-P} = 16.7 \text{ Hz}$), 144.1 (d, $J_{C-P} = 23.6 \text{ Hz}$) ppm; ${}^{31}P{}^{1}H$ NMR (162 MHz, CD₂Cl₂, 10 mM): δ = 35.2 ppm; ³¹P{¹H} NMR (162 MHz, CD₃OD): δ = 35.2 ppm; HRMS (ESI): m/z = 331.1242 ([M – I]⁺, calcd 331.1246).

8. A mixture of 7 (0.101 g, 0.22 mmol), NaPF₆ (0.740 g, 4.4 mmol), and MeCN (5 mL) was stirred at room temperature. After 1 h, the reaction mixture was concentrated under reduced pressure to obtain a solid residue. After addition of CH₂Cl₂, the precipitate was filtered, and the filtrate was evaporated under reduced pressure. MeCN (5 mL) and NaPF₆ (0.742 g, 2.3 mmol) were then added to the residue, and the resulting mixture was stirred for 1 h at room temperature. The filtration and concentration were repeated to obtain an oily residue, which was chromatographed on silica gel using CH₂Cl₂/MeOH (20/1 to 4/1) as eluents. Compound 8 was isolated as a colorless solid (53 mg, 50%) by recrystallization from CH₂Cl₂/hexane: $R_f = 0.3$ (CH₂Cl₂/MeOH = 10/1); mp 135–137 °C; IR (KBr): $\nu_{max} = 844$ (P–F) cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 10 mM): $\delta = 2.73$ (dd, J = 5.0, 5.0 Hz, 1H),

2.98-3.07 (m, 1H), 3.60-3.70 (m, 1H), 3.91-4.03 (m, 1H), 4.11-4.24 (m, 1H), 7.40-7.48 (m, 5H), 7.60-7.69 (m, 3H), 7.77–7.89 (m, 5H), 8.01 (d, J_{H-P} = 36.4 Hz, 1H), 8.02–8.06 (m, 1H) ppm; ¹H NMR (400 MHz, CD₃OD): δ = 3.34–3.44 (m, 1H), 3.82-4.05 (m, 3H), 7.40-7.47 (m, 3H), 7.55-7.60 (m, 2H), 7.61-7.70 (m, 3H), 7.79-7.89 (m, 3H), 7.90-7.97 (m, 2H), 8.06–8.11 (m, 1H), 8.31 (d, J_{H-P} = 36.8 Hz, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 24.3 (d, J_{C-P} = 47.0 Hz), 56.3 (d, $J_{\rm C-P}$ = 6.9 Hz), 116.3 (d, $J_{\rm C-P}$ = 81.2 Hz), 122.1 (d, $J_{\rm C-P}$ = 93.3 Hz), 126.5 (d, J_{C-P} = 6.8 Hz), 127.0 (d, J_{C-P} = 8.3, Hz), 129.7 (d, $J_{\rm C-P}$ = 10.6 Hz), 130.0 (s), 130.7 (d, $J_{\rm C-P}$ = 76.6 Hz), 130.7 (s), 130.8 (d, J_{C-P} = 12.9 Hz), 131.1 (d, J_{C-P} = 12.1 Hz), 132.2 (d, $J_{\rm C-P}$ = 11.4 Hz), 132.8 (d, $J_{\rm C-P}$ = 11.4 Hz), 135.6 (d, $J_{\rm C-P}$ = 3.0 Hz), 136.0 (d, J_{C-P} = 2.3 Hz), 143.4 (d, J_{C-P} = 16.7 Hz), 144.2 (d, J_{C-P} = 24.3 Hz) ppm; ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 10 mM): $\delta = -144.5$ (septet, $J_{P-F} = 712$ Hz), 34.3 ppm; ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CD₃OD): $\delta = -144.6$ (septet, $J_{P-F} = 708$ Hz), 35.2 ppm; HRMS (ESI): m/z = 331.1241 ([M - PF₆]⁺, calcd 331.1246).

9. A mixture of 3 (0.102 g, 0.238 mmol), brine, CH₂Cl₂, MeOH and MeCN was vigorously shaken in a separatory funnel at room temperature. The organic phase was separated, dried over Na₂SO₄, and evaporated to obtain a solid residue, which was chromatographed on silica gel using CH₂Cl₂/MeOH (10/1 to 5/1) as eluents. Compound 9 was isolated as a colorless solid (77.7 mg, 97%) by recrystallization from CH₂Cl₂/ hexane: $R_f = 0.12$ (CH₂Cl₂/MeOH = 10/1); mp 242-244 °C; ¹H NMR (400 MHz, CD₂Cl₂, 10 mM): δ = 3.28 (d, 3H, J_{H-P} = 14.4 Hz), 7.43-7.49 (m, 5H), 7.58-7.69 (m, 3H), 7.71-7.80 (m, 3H), 8.12 (d, 1H, J_{H-P} = 36.0 Hz), 8.23–8.30 (m, 2H), 8.84–8.89 (m, 1H) ppm; ¹H NMR (400 MHz, CD₃OD): δ = 2.93 (d, 3H, $J_{\text{H-P}} = 15.2 \text{ Hz}$, 7.42–7.48 (m, 3H), 7.55–7.60 (m, 2H), 7.63–7.67 (m, 1H), 7.68-7.73 (m, 2H), 7.83-7.97 (m, 5H), 8.01-8.05 (m, 1H), 8.40 (d, 1H, J_{H-P} = 37.2 Hz) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 7.4 (d, J_{C-P} = 48.8 Hz), 116.5 (d, J_{C-P} = 82.7 Hz), 124.2 (d, J_{C-P} = 94.0 Hz), 126.5 (d, J_{C-P} = 6.8 Hz), 126.6 (d, $J_{\rm C-P}$ = 9.1 Hz), 129.7 (d, $J_{\rm C-P}$ = 78.9 Hz), 129.8 (d, $J_{\rm C-P}$ = 11.4 Hz), 130.0 (s), 130.6 (s), 130.7 (d, J_{C-P} = 13.7 Hz), 131.3 (d, J_{C-P} = 11.3 Hz), 132.9 (d, J_{C-P} = 12.1 Hz), 133.8 (d, J_{C-P} = 12.2 Hz), 135.4 (d, J_{C-P} = 3.1 Hz), 135.6 (d, J_{C-P} = 2.3 Hz), 143.0 (d, $J_{\rm C-P}$ = 25.0 Hz), 143.9 (d, $J_{\rm C-P}$ = 16.7 Hz) ppm; ³¹P{¹H} NMR (162 MHz, CD_2Cl_2 , 10 mM): $\delta = 31.7$ ppm; ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CD₃OD): δ = 31.4 ppm; HRMS (ESI): m/z = 301.1143 $([M - Cl]^+, calcd 301.1141).$

10. A mixture of 7 (21 mg, 0.046 mmol), K₂CO₃ (21 mg, 0.15 mmol), water (1 mL), and MeOH (1 mL) was stirred for 2 h at room temperature. After addition of CH₂Cl₂ (10 mL) and water (10 mL), the aqueous layer was separated and extracted with CH₂Cl₂ (3 × 10 mL). The combined organic extracts were washed with water, dried over Na₂SO₄, and evaporated to obtain a solid residue. Compound **10** was isolated as a colorless solid (4.4 mg, 27%) by recrystallization from CH₂Cl₂/hexane: $R_{\rm f}$ = 0.5 (CH₂Cl₂/MeOH = 10/1); IR (KBr): $\nu_{\rm max}$ = 1171 (P=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.49–2.58 (m, 1H), 2.69–2.79 (m, 1H), 3.84 (dd, *J* = 6.2, 6.2 Hz, 1H), 3.97–4.07 (m, 2H), 6.90 (d, *J* = 16.0 Hz, 1H), 7.23–7.35 (m, 5H), 7.37–7.42

(m, 1H), 7.45–7.59 (m, 4H), 7.66 (d, *J* = 16.0 Hz, 1H), 7.70–7.79 (m, 4H) ppm; ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 37.2 ppm; HRMS (ESI): *m*/*z* = 349.1340 ([M + H]⁺, calcd 349.1352); UV-vis (CH₂Cl₂): λ_{max} = 309 nm (log ε = 4.22).

X-ray crystallography

Single crystals used for X-ray crystallography were grown from CH_2Cl_2 -hexane (for 3), CH_2Cl_2 -Et₂O (for 4 and 5), $CHCl_3$ -toluene (for 6) or CH_2Cl_2 -toluene (for 7 and 8). All measurements were made on a Rigaku R-AXIS RAPID diffractometer (for 3) or a Rigaku Saturn RIGAKU Saturn70 CCD system with a VariMax Mo Optic diffractometer (for 4–8) using multi-layer mirror monochromated Mo-K α radiation (0.71070 Å) at 103 K (for 3–6 and 8) or 108 K (for 7). The data were corrected for Lorentz and polarization effects. The structures were solved by using direct methods (SIR2011¹⁶ or SIR2014¹⁷) and refined by full-matrix least squares techniques against F^2 using SHELXL2013¹⁸ or SHELXL2014/7.¹⁹ The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the rigid model.

3 (CCDC 1545873†): $C_{21}H_{18}IP$, MW = 428.25, 0.14 × 0.07 × 0.06 mm, monoclinic, P_{2_1}/n , a = 9.19717(17) Å, b = 19.1790(4) Å, c = 10.65593(19) Å, $\beta = 102.343(7)^{\circ}$, V = 1836.18(8) Å³, Z = 4, $\rho_{calcd} = 1.549$ g cm⁻³, $\mu = 18.29$ cm⁻¹, collected 30.889, independent 4200, parameters 209, $R_w = 0.0523$ (all data), $R_1 = 0.0211$ ($I > 2.0\sigma(I)$), GOF = 1.145.

4 (CCDC 1545874†): C₂₁H₁₈F₆P₂, MW = 446.29, 0.11 × 0.06 × 0.05 mm, monoclinic, P_{2_1}/c , a = 11.5651(2) Å, b = 8.32080(10) Å, c = 20.4281(3) Å, $\beta = 94.8115(9)^{\circ}$, V = 1958.89(5) Å³, Z = 4, $\rho_{calcd} = 1.513$ g cm⁻³, $\mu = 2.82$ cm⁻¹, collected 32.989, independent 3843, parameters 334, $R_w = 0.01003$ (all data), $R_1 = 0.0410$ ($I > 2.0\sigma(I)$), GOF = 1.085.

5 (CCDC 1545875†): $C_{27}H_{22}Cl_2IP$, MW = 575.22, 0.08 × 0.07 × 0.03 mm, monoclinic, $P2_1/n$, a = 9.8866(2) Å, b = 21.0534(5) Å, c = 12.0079(3) Å, $\beta = 94.878(2)^{\circ}$, V = 2490.35(10) Å³, Z = 4, $\rho_{calcd} = 1.534$ g cm⁻³, $\mu = 15.77$ cm⁻¹, collected 48 571, independent 5168, parameters 280, $R_w = 0.0908$ (all data), $R_1 = 0.0377$ ($I > 2.0\sigma(I)$), GOF = 1.043.

6 (CCDC 1545876[†]): $C_{26}H_{20}F_6P_2$, MW = 508.36, 0.27 × 0.20 × 0.15 mm, monoclinic, $P2_1/c$, a = 9.1887(2) Å, b = 19.4913(3) Å, c = 13.1164(2) Å, $\beta = 101.3225(14)^\circ$, V = 2303.42(7) Å³, Z = 4, $\rho_{calcd} = 1.466$ g cm⁻³, $\mu = 2.50$ cm⁻¹, collected 35 987, independent 4396, parameters 307, $R_w = 0.0963$ (all data), $R_1 = 0.0400$ ($I > 2.0\sigma(I)$), GOF = 1.060.

7 (CCDC 1545877†): $C_{22}H_{20}IOP$, MW = 458.25, 0.40 × 0.30 × 0.10 mm, monoclinic, $P2_1/n$, a = 9.41250(10) Å, b = 22.5530(4) Å, c = 10.2457(2) Å, $\beta = 116.7384(11)^\circ$, V = 1942.39(6) Å³, Z = 4, $\rho_{calcd} = 1.567$ g cm⁻³, $\mu = 17.38$ cm⁻¹, collected 50 099, independent 4015, parameters 227, $R_w = 0.0430$ (all data), $R_1 = 0.0168$ ($I > 2.0\sigma(I)$), GOF = 1.103.

8 (CCDC 1545878†): $C_{22}H_{20}F_6OP_2$, MW = 476.32, 0.35 × 0.28 × 0.07 mm, triclinic, $P\bar{1}$, a = 9.0781(4) Å, b = 10.6021(5) Å, c = 11.4141(4) Å, $\alpha = 76.150(3)^{\circ}$, $\beta = 87.971(3)^{\circ}$, $\gamma = 86.907(3)^{\circ}$, V = 1064.79(8) Å³, Z = 2, $\rho_{calcd} = 1.486$ g cm⁻³, $\mu = 2.68$ cm⁻¹, collected 17 292, independent 4068, parameters 281, $R_w = 0.0923$ (all data), $R_1 = 0.0370$ ($I > 2.0\sigma(I)$), GOF = 1.073.

Paper

Fluorescence lifetime measurements

The fluorescence lifetimes of 3, 5, 7 and 8 were measured in CH_2Cl_2 , MeOH and H_2O at room temperature using a TCSPC system. The excitation wavelength was 374 nm (pulsed diode laser). The fluorescence lifetimes of 4 and 6 were measured using a streak camera. The excitation wavelength was 360 nm. The excitation pulse was generated by making the second harmonic pulse of the output of an optical parametric amplifier (720 nm) operated by an amplified Ti:sapphire laser system.

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