A novel bipyridine-based fluorescent host for diphenyl phosphate: affinity, photo-response and mechanism

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6,6′-Bis(hexylamino)-2,2′-bipyridine 1 exhibits an efficient blue fluorescence and the properties of 1 as a fluorescent host have been studied in various organic solutions. The host 1 shows high affinity for diphenyl phosphate 5 (K >10^4 dm^3 mol^{-1}), but only low affinity for hexanoic acid. On association with 5, 1 exists in a protonated form and forms an ion-pair type complex. In cyclohexane, blue fluorescence diminishes on association with 5, and simultaneous formation of two hydrogen bonds between amino hydrogens of 1 and phosphate oxygens contribute to stabilize the host–guest complex. In contrast, in polar solvents such as acetonitrile, a decrease in the blue fluorescence and a concomitant increase in green fluorescence from the complex is observed, and solvation to the phosphate anion stabilizes the polar ion-pair complex. These results confirm that the host 1 exhibits high affinity and selectivity with a sensitive fluorescence-response for the guest 5 both in nonpolar and polar organic solvents.

Introduction

Receptors in biological systems show not only efficient and specific molecular recognition but also an effective response, either simultaneously or subsequently. Thus, host molecules that have a built-in signalling function in their molecular structure have been extensively studied in order to design artificial receptors. Since the signalling by fluorescence has a high sensitivity and is easily detectable, fluorescent hosts have drawn considerable interest.[1]

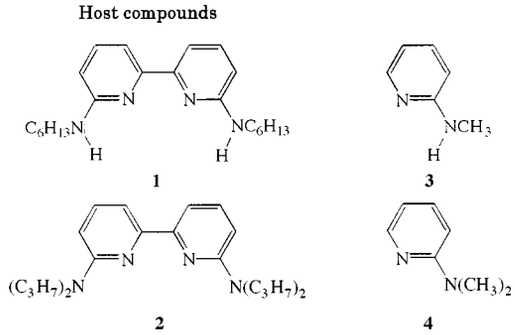
Until now, various types of fluorescent hosts have been reported. The most common host design involves the introduction of environmentally-sensitive fluorophore(s) as auxiliaries in order to detect microenvironmental changes induced by host–guest association.[2] Other hosts utilize fluorescence sensitization, quenching by energy[3] or electron transfer.[4] However, these types of fluorescent host are generally sensitive to factors other than host–guest association.

Among other types of fluorescent hosts, hydrogen-bonding of guest molecules to a fluorescent moiety in the host offers a more direct method of monitoring the host–guest association.[5] However, changes in fluorescence were generally limited.

2,2′-Bipyridine (bpy) and its derivatives are well-known as chelating agents, and serve as essential building-blocks for various functional transition-metal complexes. Among them, bpy-containing ruthenium(II) complexes show characteristic emission, and have been the subject of intense studies. However, bpy and its derivatives are generally non-fluorescent,[6] and relatively little is known about their fluorescent properties.[7] We recently reported that bpy derivatives bearing an amino group at the 6-position exhibit blue fluorescence with high quantum yield.[8] The compounds have two basic ring nitrogens and amino group(s) at the 6(6′)-position(s). Therefore, these novel fluorescent compounds are prone to interaction with other molecules by electrostatic and/or hydrogen-bonding interactions, which might alter directly their fluorescent properties.

Phosphoric acid diesters are an important class of biological substances, and are known to show a variety of physiological activities. In this study, we selected diphenyl phosphate as a model guest compound, and studied the properties and photo-response of 6,6′-bis(hexylamino)-2,2′-bipyridine **1** as a novel fluorescent host. The host showed high affinity and sensitivity toward the guest both in polar and nonpolar solvents.

Host compounds



Guest compounds

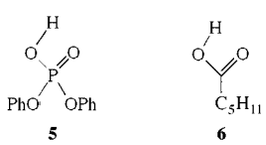


Fig. 1 Structures of hosts **1**–**4** and guests **5**, **6**

Results

Properties of the hosts 1–4

Fig. 1 shows the structures of bipyridine hosts **1** and **2** possessing two amino groups at the 6,6′-positions. The amino groups of the host **1** are monoalkylated, while those of the host **2** are fully alkylated. Pyridine hosts **3** and **4** have also been examined as reference compounds for the hosts **1** and **2**. The bipyridine hosts **1** and **2** showed π–π* absorption at around 350 nm both in acetonitrile and cyclohexane, and excitation of any of the absorption bands caused blue fluorescence with high efficiency (Table 1). Deaeration of the solution hardly affected the fluorescence, confirming that the fluorescence was not affected by dissolved oxygen. The fluorescence intensity of these hosts increased linearly with their concentration, and their excitation spectra monitored at 500 nm coincided well with their absorption spectra. These spectroscopic properties of the hosts **1** and **2** are essentially the same as those of their parent compound, 6,6′-diamino-2,2′-bipyridine, which shows similar fluorescence from the lowest π* orbital.[8]

The basicity of the ring nitrogen was determined by spectral

Table 1 Absorption and fluorescence maxima of **1**–**4** at 20 °C

		Cyclohexane		Acetonitrile	
Host	pK_a[a]	λ_{abs}/nm (log ε)	λ_{em}/nm (Φ)	λ_{abs}/nm (log ε)	λ_{em}/nm (Φ)
1	6.4	340.5 (4.136)	385 (0.35)	343.0 (4.090)	402 (0.30)
2	6.3	352.5 (4.096)	399 (0.45)	355.0 (4.051)	422 (0.33)
3	6.4	299.0 (3.571)	335 (0.31)	307.0 (3.542)	360 (0.28)
4	6.3	309.0 (3.562)	347 (0.25)	312.0 (3.516)	372 (0.20)

[a] Determined in water–dioxane (1:1).

Table 2 Binding constants (K/dm^3 mol^{-1}) for **1** with guests at 20 °C

	Cyclohexane		Acetonitrile	
Guest	Abs[a]	Fl[b]	Abs[a]	Fl[b]
5	*c*	1.7×10^7	*c*	1.7×10^7
Triethyl phosphate	1×10	2×10	0	0
6	6.7×10	7.7×10	~1	~1
Methyl hexanoate	0	0	0	0
Hexan-2-one	<10	<10	0	0
Hexan-1-ol	<10	<10	0	0

[a] Determined from absorption change. [b] Determined from fluorescence change. [c] Too large (>10^6 dm^3 mol^{-1}) to be determined.

titration in water–dioxane (1:1) solution (Table 1). The pK_a values of **1**–**4** were 6.3 or 6.4, showing that the basicity of the ring nitrogen was almost the same.

Guest affinity of host 1

The binding ability of **1** with guest compounds was studied in cyclohexane at 20 °C. Increase in diphenyl phosphate **5** concentration caused a quantitative change in the absorption spectrum of **1** (3.1×10^{-5} mol dm^{-3}) with isosbestic points at 299 and 362 nm until the molar ratio of **1** and **5** reached 1:1 (Fig. 2). The final spectrum was identical to that of a hydrochloride salt of **1**, showing that the spectral change was due to protonation of the host by **5**. The binding constant was too large to be determined in this concentration range. Fluorescence of **1**, whose concentration (2.8×10^{-7} mol dm^{-3}) was approximately 10^{-2} times lower than that for the absorption spectral measurement, was measured by excitation of one of the isosbestic points at 299 nm. Addition of **5** caused a considerable decrease in the fluorescence at 382 nm, and a small green fluorescence appeared at 502 nm. The guest **5** has no absorption above 280 nm, and deaeration hardly affected the observed decrease in blue fluorescence on addition of **5**. Since the excitation spectrum of the green fluorescence was identical to the absorption spectrum of the hydrochloride salt of **1**, the green fluorescence must originate from the protonated species of **1**. The observed decrease and increase of the fluorescence at 382 and 502 nm, respectively, fitted well the calculated decreasing and increasing curves by assuming 1:1 stoichiometry. Therefore, it was concluded that the observed fluorescence spectral change was due to the 1:1 association of **1** and **5**, and the binding constants were determined to be 1.7×10^7 and 1.6×10^7 dm^3 mol^{-1} from the decrease and increase in the fluorescence, respectively (Table 2).

Addition of large, excess amounts of triethyl phosphate (1×10^{-1} mol dm^{-3}) possessing no acidic proton caused only small changes in the absorption and fluorescence spectra of **1**. The binding constant with **1** (2×10 dm^3 mol^{-1}) was nearly 10^6 times smaller than that for **5**. Since the host **1** existed in the protonated form on association with **5**, the presence of an acidic proton in the guest molecule is essential for strong binding.

In the case of hexanoic acid **6** possessing an acidic proton (pK_a = 4.8) weaker than **5** (pK_a = 1.9), only a moderate spectral change was observed. The absorption spectral change was different from that with **5**, and only a decrease in the blue fluorescence was observed (Fig. 3). Therefore, protonation of **1** was

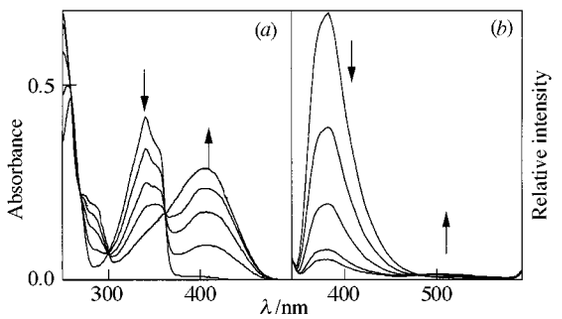


Fig. 2 Spectral titration of **1** with **5** in cyclohexane at 20 °C. (*a*) Absorption spectra. Concentrations of **1** and **5** were 3.1×10^{-5} and 0–3.1×10^{-5} mol dm^{-3}, respectively. (*b*) Fluorescence spectra (λ_{ex} = 299 nm). Concentrations of **1** and **5** were 2.8×10^{-7} and 0–8.0×10^{-7} mol dm^{-3}, respectively.

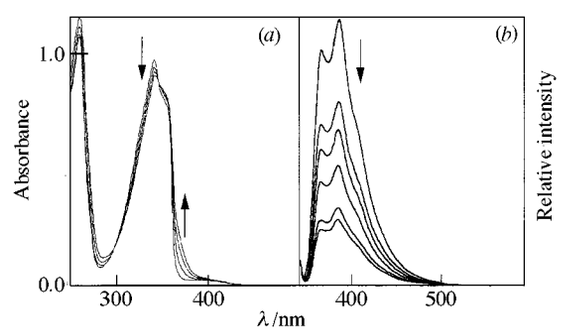


Fig. 3 Spectral titration of **1** with **6** in cyclohexane at 20 °C. (*a*) Absorption spectra. Concentrations of **1** and **6** were 6.0×10^{-5} and 0–4.0×10^{-2} mol dm^{-3}, respectively. (*b*) Fluorescence spectra (λ_{ex} = 348 nm). Concentrations of **1** and **5** were 6.0×10^{-6} and 0–4.0×10^{-2} mol dm^{-3}, respectively.

unlikely to occur by addition of **6**. The binding constant of **1** with **6** was determined to be smaller than 10^2 dm^3 mol^{-1} from either absorption or fluorescence spectral changes, which were 10^5 times lower than with **5**. Hardly any affinity was observed for other C_6-guests such as methyl hexanoate, hexan-2-one and hexan-1-ol.

When acetonitrile (higher polarity) was used as a solvent, the host **1** showed different association behaviour with the guest molecules. Absorption spectral titration of the host **1** (2.7×10^{-5} mol dm^{-3}) by **5** indicated quantitative association of **1** with **5** up to a molar ratio of 1:1. The spectral change was essentially the same as that in cyclohexane (Fig. 4), indicating the protonation of **1** by addition of **5**. However, green fluorescence from the protonated species of **1** was much stronger in acetonitrile and increased drastically as the blue fluorescence diminished (Fig. 4). The binding constants determined from the green and blue fluorescence were in good agreement and were large enough (Table 4). Therefore, the host **1** exhibits high affinity for the guest **5** in both polar and non-polar solvents. However, the host **1** exhibited almost no affinity for other guests as presented in Table 2.

^{1}H NMR study of association of the host 1 with 5

2,2′-Bipyridine (bpy) has a predominantly s-*trans* conformation

Table 3 Chemical shifts in the ^{1}H NMR spectrum of **1** with **5**

		3H	4H	5H	|3H-5H|	NH
1	[$^2H_6$]Benzene	8.23	7.36	6.04	2.19	4.04
1 + **5** (1:1)		7.69	*a*	6.47	1.22	*b*
1	[$^2H_3$]Acetonitrile	7.33	7.24	6.20	1.13	4.92
1 + **5** (1:1)		6.92	7.35	6.34	0.58	*b*

[a] Unable to be determined because of the resonance peaks of **5**. [b] Not detected.

Table 4 Binding constants (K/dm^3 mol^{-1}) for hosts **1**–**4** with **5** at 20 °C

	Cyclohexane			Acetonitrile		
Host	Abs[a]	Fl (Dec)[b]	Fl (Inc)[c]	Abs[a]	Fl (Dec)[b]	Fl (Inc)[c]
1	*d*	1.7×10^7	1.6×10^7	*d*	1.5×10^7	1.7×10^7
2	2.0×10^2	2.8×10^2	2.1×10^2	*d*	4.0×10^6	4.2×10^6
3	$>1 \times 10^5$	2.7×10^5	2.6×10^5	*d*	2.7×10^6	2.7×10^6
4	1.0×10^3	1.1×10^3	*e*	*d*	1.9×10^6	*e*

[a] Determined from absorption change. [b] Determined from decrease in the fluorescence. [c] Determined from increase in the fluorescence. [d] Too large ($>10^6$ dm^3 mol^{-1}) to be determined. [e] Not detected.

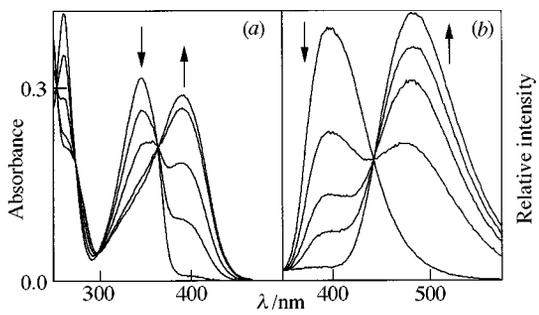


Fig. 4 Spectral titration of **1** with **5** in acetonitrile at 20 °C. (*a*) Absorption spectra. Concentrations of **1** and **5** were 2.7×10^{-5} and 0–2.7×10^{-5} mol dm^{-3}, respectively. (*b*) Fluorescence spectra ($\lambda_{ex} = 298$ nm). Concentrations of **1** and **5** were 2.9×10^{-7} and 0–1.8×10^{-6} mol dm^{-3}, respectively.

in organic solution, and its 3,3′-protons are known to show an anomalous downfield shift compared to the other β-protons, the 5,5′-protons.[9] The ring current effect of the neighbouring pyridine ring and the electrostatic field effect of the nitrogen lone pair electrons are reported to be responsible for this downfield shift.[9] In contrast, the monoprotonated species is in the s-*cis* conformation and the 3,3′-protons appeared on the upfield side due to the absence of the effect of the nitrogen lone pair and the 5,5′-protons shifted to the downfield side.

Table 3 shows ^{1}H NMR chemical shifts (δ) of **1** (5×10^{-3} mol dm^{-3}) and **1** + **5** (1:1) in [$^2H_6$]benzene and [$^2H_3$]acetonitrile. In this experiment, [$^2H_6$]benzene was used as a nonpolar solvent because of the low solubility of the guest **5** in cyclohexane. The chemical shift of the 3,3′-protons of **1** were shifted upfield, whereas the 5,5′-protons showed a small downfield shift. Therefore, the results indicated that the conformation of **1** on association with **5** was s-*cis* in both nonpolar and polar solvents.

It is worth noting that the amino proton signals disappeared on addition of **5**, indicating that the amino group was involved in complex formation with **5**.

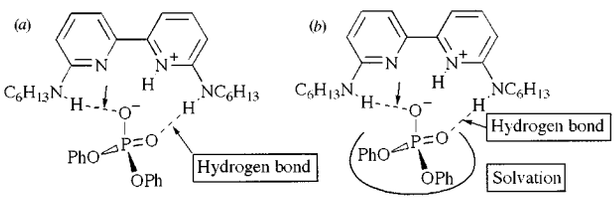
Affinity of hosts 1–4 for diphenyl phosphate

To understand the high affinity of the host **1** for **5** both in cyclohexane and acetonitrile, we studied the affinity of the other bipyridine host **2**, whose amino groups were fully alkylated. The pyridine hosts **3** and **4** were also examined as the reference. An increase in the concentration of **5** in both cyclohexane and acetonitrile caused absorption and fluorescence spectral alteration of the hosts **2**–**4**, which indicated the formation of 1:1 complexes by protonation with the ring nitrogens

Table 5 Binding constants (K/dm^3 mol^{-1}) with **5** at 20 °C

Host		Cyclohexane	THF[a]	Acetone	Acetonitrile	DCM[b]
1	Abs[c]	*e*	2.0×10^4	$>1 \times 10^5$	*e*	*e*
	Fl[d]	1.7×10^7	3.0×10^4	3.2×10^5	1.7×10^7	4.5×10^7
2	Abs[c]	2.1×10^2	1×10	2.8×10^3	*e*	*e*
	Fl[d]	2.0×10^2	1×10	9.1×10^3	4.2×10^6	6.6×10^6

[a] THF: tetrahydrofuran. [b] DCM: dichloromethane. [c] Determined from absorption change. [d] Determined from fluorescence change. [e] Too large ($>10^6$ dm^3 mol^{-1}) to be determined.



Scheme 1 Proposed structure of the complexes **1** and **5**; (*a*) in cyclohexane; (*b*) in acetonitrile

of the hosts. Binding constants determined from the observed change of absorption and fluorescence spectra agreed with each other (Table 4).

In cyclohexane, the binding constant of **1** bearing the amino hydrogens is 10^5 times larger than that of **2** possessing no amino hydrogen (Table 4). Similarly, the pyridine host **3** possessing a secondary amino group showed a 10^2 times larger binding constant than **4**. Since the basicity of the ring nitrogens is almost the same (Table 1), the amino hydrogen plays a vital role in the formation of a stable complex with **5** in cyclohexane. Comparison of the binding constants of **1** and **3** clarifies the role of the bipyridine structure. The bipyridine host **1** with two aminopyridine units showed a binding constant not twice but 10^2 times larger than the aminopyridine host **3**. Therefore, the bipyridine structure of the host **1** showed a large cooperative effect on association with **5** in cyclohexane.

In acetonitrile, however, the binding constants were less dependent on the structure of the host, and the affinities of the hosts **2** and **4** became much higher. The host **1** still showed high affinity ($K = 1.7 \times 10^7$ dm^3 mol^{-1}) but only four times larger than that of **2**. Similarly, the pyridine host **3** showed only a twice higher affinity than **4**, showing a smaller contribution of the amino hydrogen in a polar solvent. Moreover, the cooperative effect of the bipyridine structure became less evident, and the host **1** showed only a 6 times higher affinity than its pyridine-type analogue **3**.

Further examination of the binding constant of **1** and **2** with **5** in other organic solvents were carried out and the results are summarized in Table 5. The fluorescence of **1** was significantly changed by addition of **5** and large binding constants ($K > 10^4$ dm^3 mol^{-1}) were observed in every solution regardless of the polarity of the solvent. On the contrary, host **2** with no amino hydrogen displayed a poor ability for binding with **5**, especially in cyclohexane and THF.

Discussion

Structure of the host–guest complex and origin of the high affinity of the bipyridine host 1 with diphenyl phosphate 5

The bipyridine host **1** displayed a high affinity for diphenyl phosphate **5** in various organic solvents. Association of the host **1** with **5** led to the formation of a 1:1 complex in which one of the ring nitrogens of the host was protonated, as evidenced by the absorption and ^{1}H NMR spectra. Therefore, the complex is the ion-pair of the host **1** and **5**. In cyclohexane the host **1** showed nearly 10^5 times higher affinity for **5** than the host **2**,

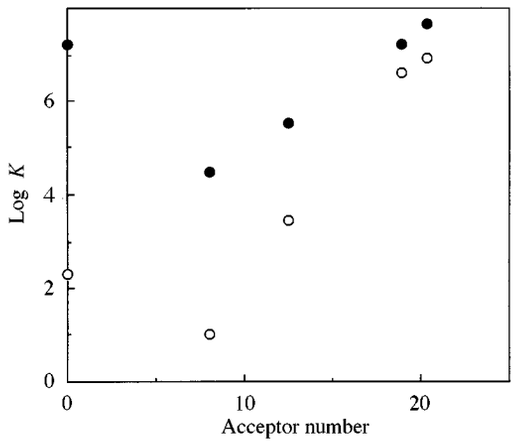


Fig. 5 Plot of log *K* *vs.* acceptor number (AN) of organic solvents. ●: **1** + **5**; ○: **2** + **5**.

though the pK_a values of the ring nitrogens are almost the same, and this difference is ascribed to the presence of amino hydrogens in the host **1**. The conformation of the host **1** in the complex was s-*cis*, and disappearance of the amino proton signal suggested that the amino protons were involved in the complex formation. Studies on the structure of the complex using the CPK model and molecular mechanics calculations showed that the two oxygens of the phosphate anion and the amino hydrogens of the host **1** in the s-*cis* conformation could be placed close enough to form two hydrogen bonds simultaneously without any noticeable steric problem [Scheme 1(*a*)]. In the optimized structure of the complex of **1** and **5** (by molecular mechanics calculations), the hydrogen bond length between the amino hydrogens and the phosphate oxygens was 0.18–0.19 nm, which is consistent with the reported values.[10] Since **2** has no amino hydrogen, such a stabilization mechanism cannot be expected and this resulted in a low binding constant with **5**. This structural model also explains the observed cooperative effect of the two aminopyridine units in the host **1**. The pyridine host **3** has one amino hydrogen and can form only one hydrogen bond with the guest **5**. In contrast, the host **1** can form two hydrogen bonds simultaneously, which resulted in a 10^2 times larger binding constant compared to that of the host **3**.

From the difference of the binding constants of **1** (K_1) and **2** (K_2) with **5**, we estimated the hydrogen bond strength in the complex. By assuming that the entropy changes upon complex formation of **1** and **2** with **5** are the same, the enthalpy gain[11] due to the formation of the two hydrogen bonds is estimated to be -27 kJ mol^{-1}. Therefore, the strength of each hydrogen bond is estimated to be -13.5 kJ mol^{-1}, and is comparable to other hydrogen bonding interactions.[12] Similarly, the contribution of the hydrogen bond to the complexation of **3** with **5** is estimated from the difference between the binding constants of **3** and **4** to be -13 kJ mol^{-1}, which is in good agreement with the value obtained from the bipyridine hosts. These results further support the simultaneous formation of two hydrogen bonds in the complex of **1** and **5**, and this is the origin of the cooperative effect in the bipyridine structure.

In acetonitrile, however, the affinity of the host **2** for the guest **5** became much higher, and the binding constant of **1** was only four times larger than that of **2**. Since the structure of the host–guest complex was the ion-pair type and not much different from that in cyclohexane, polar solvents such as acetonitrile greatly contribute towards the stabilization of the polar ion-pair complex of the host and guest. Thus, the contribution of the hydrogen bonds in the stabilization of the complex was much smaller than in cyclohexane, and the log *K* values of the hosts **1**–**4** with similar pK_a values are not much different from each other though the host **1** still showed 4 to 8 times higher affinity (Table 2). To further examine the effect of polar solvents, log *K* values of the host **1** and **2** with **5** in various solvents are plotted *vs.* acceptor number (AN) and donor number (DN) of the solvents. Except for cyclohexane, good correlation was observed between log *K* and AN, which is shown in Fig. 5, but not with DN. This indicates that solvation to the phosphate anion is important for stabilization of the highly polar ion-pair complex [Scheme 1(*b*)].

Thus, it is shown that the complex between **1** and **5** is stabilized by hydrogen bonding interaction and solvation to the phosphate anion. In nonpolar solvents such as cyclohexane, the contribution of the solvation effect greatly decreased but the contribution of the hydrogen bonding was large enough to show high guest affinity. In contrast, in polar solvents like acetonitrile, contribution of the hydrogen bonds becomes smaller but solvation of the polar solvent contributes to the high affinity. Since hydrogen bond formation is more effective in solvents with lower AN, in which electrostatic interaction becomes less effective, the two stabilization processes should operate in a complementary fashion to ensure a high affinity for **5**.

The host 1 as a fluorescent probe for diphenyl phosphate 5

The host **1** showed high affinity for diphenyl phosphate **5** both in polar and nonpolar organic solutions. The host **1** existed in the protonated form on association with the guest **5**, and the absorption and fluorescence of the host **1** were greatly altered. Since the fluorescence of the host has a strong intensity (quantum yield: 0.3–0.35), is not sensitive to the dissolved oxygen, appears in the visible region, and alters drastically on association with the guest **5**, the host **1** seems to be the most suitable and sensitive probe for monitoring phosphoric acid diester by fluorescent methods in organic solvents. Especially in the acetonitrile and dichloromethane, the green fluorescence of the host–guest complex becomes strong enough and comparable to the blue fluorescence of the host **1**, and the host–guest association can easily be monitored by fluorescence colour change from blue to green.

The host **1** showed only small affinity for the carboxylic acid guest **6**, and practically no affinity for phosphoric acid triester, carboxylic acid ester, and other substrates possessing no acidic protons (Table 2). Therefore, the host **1** has a high selectivity for phosphoric acid diester in organic solvents.

There are a variety of lipophilic biomolecules with acidic protons such as lipids and lipoproteins. Among them, carboxylic acid and phosphoric acid derivatives are the major class of lipophilic acidic substrates, and are indispensable for many important physiological activities. The host **1** showed a photoresponse only for phosphoric acid diester but not for carboxylic acid in various organic solvents, and can therefore be a useful fluorescent monitor for phospholipid and other biologically-important lipophilic phosphoric acid diesters.

In conclusion, the host **1** reported in this study shows high sensitivity and selectivity for phosphoric acid diester in organic solvents and has the ability to signal host–guest recognition by fluorescence. Because of the importance of phosphate derivatives in living systems, phosphate receptors have been actively studied.[13] Since the signalling by fluorescence has high sensitivity and is easily detectable, the aminobipyridine unit, which shows efficient fluorescence and has several sites for intermolecular interactions, can be a useful building block in the design of novel and efficient phosphate receptors.

Experimental

Materials

2,2′-Bipyridine derivatives **1** and **2** were synthesized as previously reported.[8] 2-(Methylamino)pyridine **3**, 2-(dimethylamino)pyridine **4** and hexanoic acid **6** were purchased from Aldrich Chem. Co. and diphenyl phosphate **5** from TCI. Spectrometric grade solvents were used for the measurements.

Methods

The UV–VIS absorption spectra were measured with a JASCO Ubest-50 or a SHIMADZU UV-2500PC spectrophotometer and fluorescence spectra were obtained with a JASCO FP-770 or a SHIMADZU RF-5300PC spectrofluorometer at 20 °C. ^{1}H NMR spectra were recorded on a JEOL GX-270 spectrometer in [$^2H_6$]benzene and [$^2H_3$]acetonitrile at 25 °C with tetramethylsilane as an internal standard. The pK_a values of the hosts **1**–**4** were determined spectrophotometrically in water–dioxane (1:1), by addition of small amounts of concentrated sulfuric acid aqueous solution.

Binding constants were determined by spectroscopic titration at 20 °C using a least-squares curve fitting method. To a host solution (3×10^{-5} mol dm^{-3}) was added, successively, a small amount of concentrated guest solution and the observed change in the absorption spectra was followed at 350 nm. For fluorescence titration of the hosts (3×10^{-7} mol dm^{-3}) at 20 °C, decrease and increase in the fluorescence intensities were monitored at 380–410 and 500 nm, respectively.

Molecular mechanics calculations were performed with a CAChe system on an Apple Macintosh PC.

Acknowledgements

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