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Solvent-dependent conformational and fluorescence change of an *N*-phenylbenzohydroxamic acid derivative bearing two pyrene moieties

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ABSTRACT

The conformation of *N*-phenylbenzohydroxamic acid has been reported to change depending on the solvent properties. Here, we newly synthesized *N*-phenylbenzohydroxamic acid derivative, which contains two pyrene moieties separated from the phenyl rings by ethylene linkers. It showed solvent-dependent conformational change, and its fluorescence was also solvent-dependent, that is, only monomer fluorescence of pyrene was observed in DMSO or DMF, whereas the excimer fluorescence was observed in CH_2Cl_2 or $CHCl_3$. Thus, the structural characteristics could be converted to fluorescence change as output, which would be a good candidate as a fluorescent sensor.

1. Introduction

A molecular switch is a molecular system that can be reversibly interconverted between two or more stable states when exposed to a stimulus, such as light, electrical potential or chemical reaction.[1] A number of polymers or supramolecules that change their three-dimensional structures and functions in response to external stimuli have been developed.[2] There are also various switching systems based on structural change of small molecules, such as cyclization of 1,2-diarylethenes and isomerization of azobenzenes.[3] Generally, the energy barriers between the two different structures are sufficiently high that the structures can be clearly distinguished, though in some cases, interconversion between conformers with a rather small energy barrier has been used. When the interconversion between the conformers occurs in response to some chemical interaction or change of environmental conditions, and results in a change of the measurable properties, the molecule has potential utility as a sensor molecule.

We have previously reported the conformational alteration of aromatic amides caused by *N*-methylation. Thus, benzanilide (**1a**) exists in trans form both in the crystal and in various solvents, while *N*-methylbenzanilide (**2a**) exists in cis form in the crystal and predominantly in cis form (98.3% in CD_2Cl_2 at 198 K) in solution (Fig. 1).[4] The cis conformational preference is general for various *N*-methylated amides, and also for *N*-methylated thioamides, amidines, ureas, thioureas, and guanidines, and can be applied to the

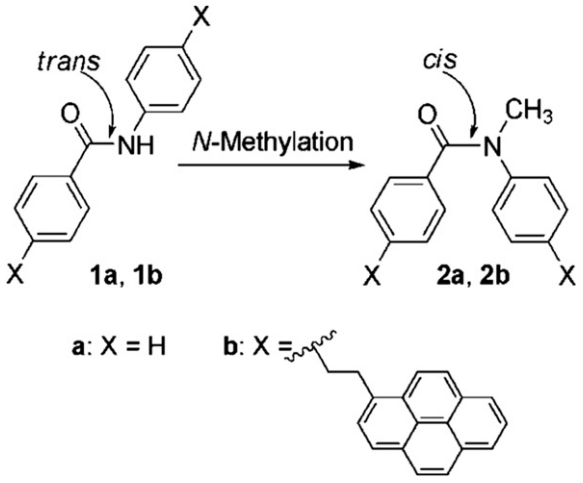

Fig. 1. Conformational alteration of aromatic amides by *N*-methylation.

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construction of aromatic molecules with unique three-dimensional structures.[5]

In addition, we also found that *N*-phenylbenzohydroxamic acid (**3**, *N*-hydroxy derivative of benzanilide) changed its conformation solvent-dependently (Fig. 2); it existed predominantly in cis form (>98%) in CD_2Cl_2, while the percentage of the cis isomer decreased to 49% in methanol-d_4, and the trans conformer was predominant (77%) in acetone-d_6.[6,7] Interestingly, two types of crystal structures were obtained depending on the recrystallization solvent, and the structure corresponded to that of the major conformer in each solvent. These results indicated that the *N*-hydroxybenzanilide structure could be used as a solvent-dependent switch. In this paper, we studied the applicability of this structural characteristic to the development of fluorescent sensor by introduction of fluorophores to this structure.

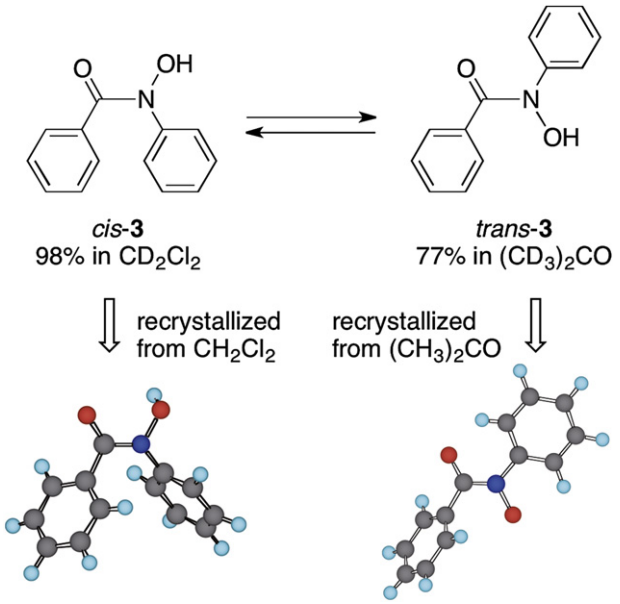


Fig. 2. Solvent-dependent conformational change of *N*-phenylbenzohydroxamic acid **3**.

2. Results

Pyrene is a polycyclic aromatic molecule with fluorescence at 370–390 nm; however, when the excimer is formed, it exhibits fluorescence with longer wavelength (ca. 480 nm).[8,9] In our previous work, we showed that the conformational difference between aromatic secondary and tertiary amides could be visualized by the introduction of two pyrene units, at the *para* position to the amide group on each aryl ring, via an ethylene linker; that is, monomer fluorescence of pyrene was observed in the extended trans-form of the benzanilide moiety (**1b**), while the folded cis-form of *N*-methylbenzanilide (**2b**) showed excimer fluorescence (Fig. 1).[10] Based on that work, we designed compound **4** as a candidate molecule with solvent-dependent fluorescence, in which the excimer fluorescence is expected to be observed only when the compound exists in cis conformation, like *N*-methylbenzanilide (**2b**), while monomer fluorescence would be major in the trans conformation (Fig. 3).

The synthesis of compound **4** is illustrated in Scheme 1. 1-Bromopyrene (**5**) was reacted with trimethylsilylacetylene by means of the Sonogashira coupling reaction (99%), followed by deprotection (57%) with potassium fluoride to give 1-ethynylpyrene (**7**).[11] 4-Iodobenzoic acid (**8**) was converted to the acid chloride, which was reacted with *N*-(4-iodophenyl)hydroxylamine in the presence of pyridine to afford 4,4′-diiodo-*N*-

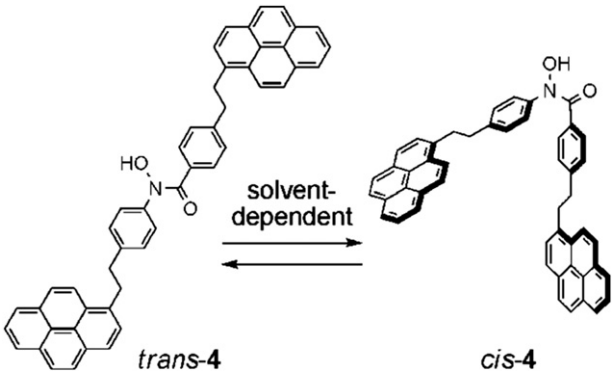
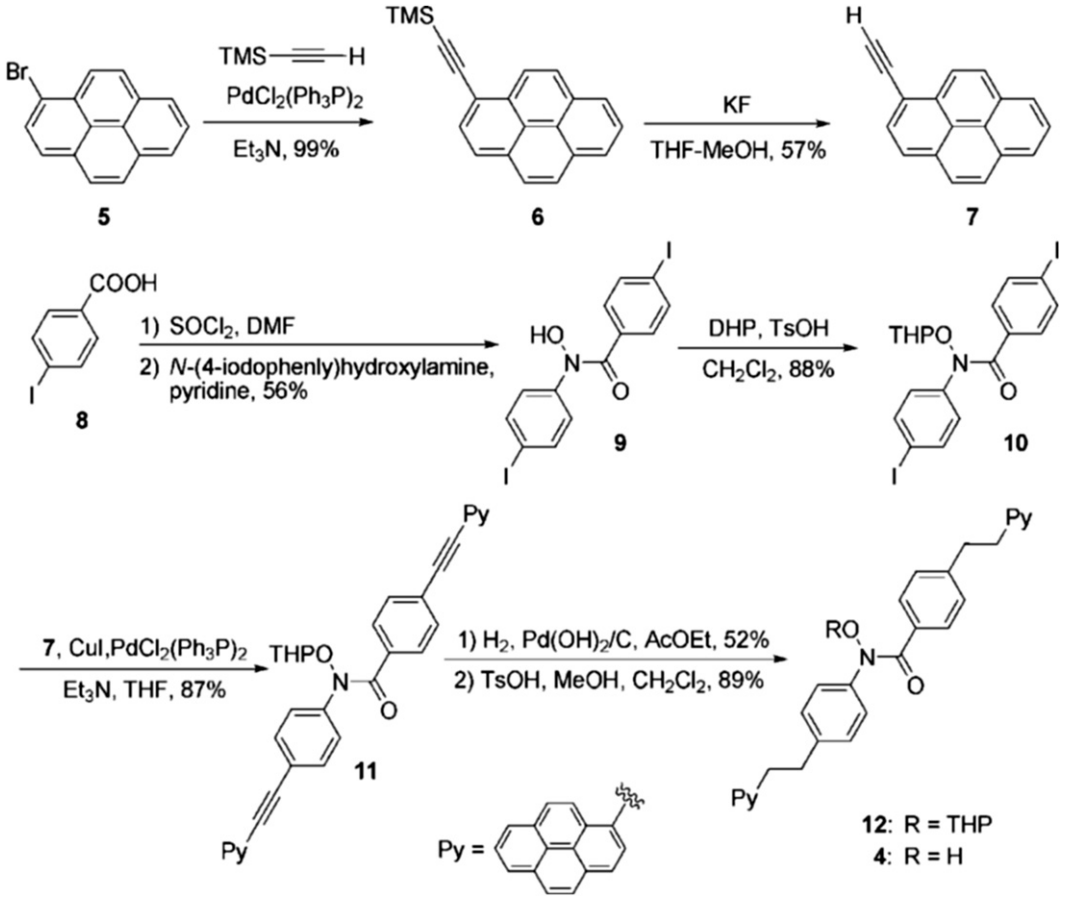


Fig. 3. Structure of *N*-phenylbenzohydroxamic acid derivative **4**.

phenylbenzohydroxamic acid (**9**) in 56% yield. After protection (88%) of the hydroxy group of **9**, Sonogashira reaction of compound **10** with 1-ethynylpyrene (**7**) in the presence of copper(I) iodide and $PdCl_2(PPh_3)_2$ gave the bis(pyrenyl) compound **11** in 87% yield.[12] Finally, hydrogenation (52%) followed by deprotection (89%) gave compound **4**.

The conformation of compound **4** was examined in various solvents by means of ^{1}H NMR spectroscopy (Fig. 4). In order to distinguish the solvent-dependent change in the ratio of the cis/trans conformers from simple solvent effects on the chemical shifts, the ^{1}H NMR spectra of methyl 4-[2-(1-pyrenyl)ethyl]benzoate (**13**)[10] were also measured. The signals of the aromatic protons ortho (marked by closed circle in Fig. 4g–l) to the ester group of **13** were only slightly shifted (7.9–8.0 ppm) due to the solvent effect. The ^{1}H NMR spectra of compound **4** at 298 K showed one set of signals in each solvent (Fig. 4a–f), while there were two sets of signals, corresponding to trans and cis conformers of **4**, at 193 K in acetone-d_6 and THF-d_8 and at 223 K in DMF-d_7 (Fig. S1). These signals could be assigned to individual conformers by comparison with the reported chemical shifts of *N*-phenylbenzohydroxamic acid (**3**). The ratio of the cis isomer is 50% in acetone-d_6 (193 K), 28% in THF-d_8(193 K), and 21% in DMF-d_7 (223 K) (Table 1). The ^{1}H NMR spectra of **4** in CD_2Cl_2 and $CDCl_3$ showed only one set of signals even at 183 K or 223 K, respectively (Fig. S1); that is, the chemical shifts of the protons on the two phenyl groups were observed only at higher field (7.3 ppm for the protons at the *ortho* position to the carbonyl groups, marked by closed circle, and around 7.1 ppm for others, marked by open diamond, Fig. 4a and b). Like *N*-phenylbenzohydroxamic acid (**3**), compound **4** existed predominantly in cis form (>99%) in CD_2Cl_2 and $CDCl_3$. In DMSO-d_6, the proton signals of the phenyl rings were observed at lower field at 298 K, being similar to those in THF-d_8. Therefore, compound **4** appears to exist mainly in trans form in these solvents.

The fluorescence spectra of compound **4** in various solvents were examined (Fig. 5 and Table 1). Compound **4** emitted some fluorescence in every solvent examined, and the spectral shape varied depending on the solvent. In DMSO and DMF, compound **4** showed similar spectra to those of the control compound **13**, which has one pyrene moiety (Fig. S2); that is, vibrational fluorescence at 370–390 nm, which could correspond to the monomer fluorescence of pyrene, was strong, while little excimer fluorescence at around 480 nm was observed (Fig. 5a and b). Excimer fluorescence appeared weakly in THF, was a little increased in acetone, and became stronger intensity in CH_2Cl_2 and $CHCl_3$ (Fig. 5c–f). The ratio of the fluorescence intensity at 470 nm to that at 398 nm was 0.05, 0.05, 0.07, 0.15, 0.22, and 0.27 for DMSO, DMF, THF, acetone, $CHCl_3$, and CH_2Cl_2, respectively (Table 1). The spectral shape in each solvent examined did not change in the concentration range from 1.25 μM to 5.0 μM, and therefore intermolecular interaction would not be significant under these conditions.



Scheme 1. Synthesis of compound **4**.

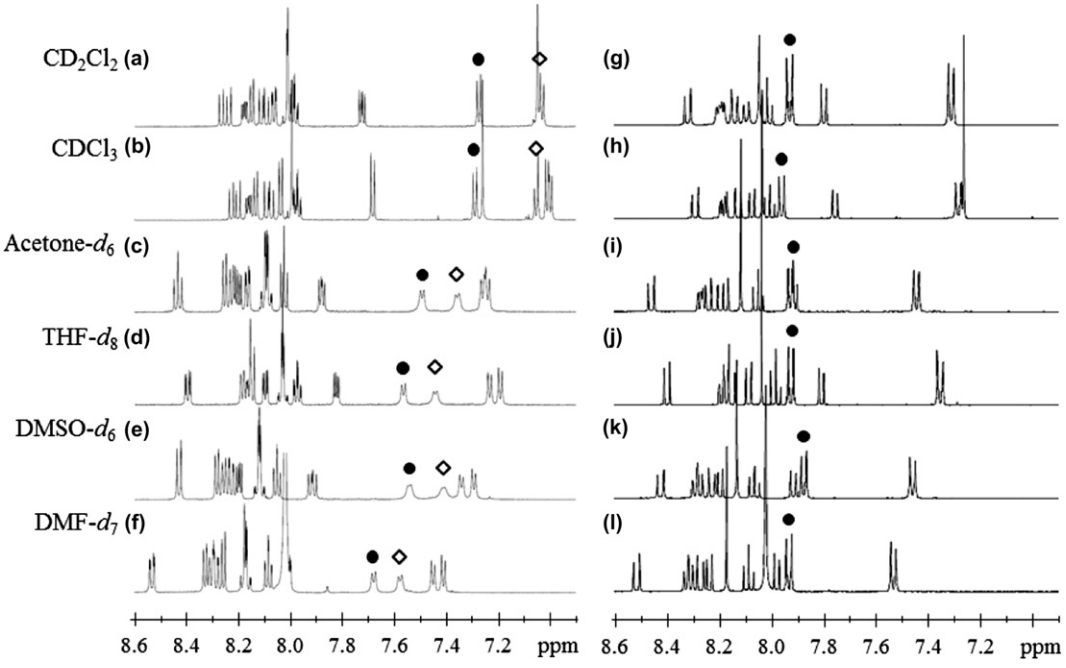


Fig. 4. ^{1}H NMR spectra (aromatic region, 6.9–8.6 ppm) of compound **4** (a–f) and methyl 4-[2-(1-pyrenyl)ethyl]benzoate (**13**, g–l) in various solvents at 298 K. The marked signals are due to protons *ortho* to the amide carbonyl group (closed circle) or nitrogen atom (open diamond).

Table 1
Fluorescence properties of compound **4** in various solvents

Solvent	Ratio of cis/trans[a]	Ratio of excimer/monomer fluorescence intensity[c]
DMSO	(Trans major)[b]	0.05
DMF	Cis 21%	0.05
THF	Cis 28%	0.07
Acetone	Cis 50%	0.15
$CHCl_3$	Cis only	0.22
CH_2Cl_2	Cis only	0.27

[a] The ratio was determined by means of ^{1}H NMR spectroscopy in deuterated solvents. Temperature was 183 K for CD_2Cl_2, 193 K for acetone-d_6 and THF-d_8, and 223 K for DMF-d_7 and $CDCl_3$.
[b] The trans conformer is major, although the cis/trans ratio could not be determined.
[c] Ratio of fluorescence intensities at 470 nm/398 nm for 5 μM of compound **4** (λ_{ex}: 345 nm).

These data suggested that compound **4** shows solvent-dependent fluorescence, i.e., the ratio of the excimer fluorescence was increased in less polar solvents such as CH_2Cl_2 and $CHCl_3$, whereas monomer fluorescence was observed almost exclusively in polar solvents, such as DMSO and DMF. These characteristics are presumably derived from the solvent-dependent cis/trans structural alteration deduced from the NMR study (Fig. 4, Table 1).

3. Discussion

N-Phenylbenzohydroxamic acid (**3**) shows solvent-dependent conformational change, and exists as the cis conformer in CD_2Cl_2, while the ratio of the cis conformer is decreased in more polar solvents, such as acetone-d_6 and methanol-d_4. Compound **4**, developed in this study, showed similar structural property to compound **3** (Table 1). In fluorescence spectra, compound **4** emitted little excimer fluorescence in polar solvents such as DMF and THF,

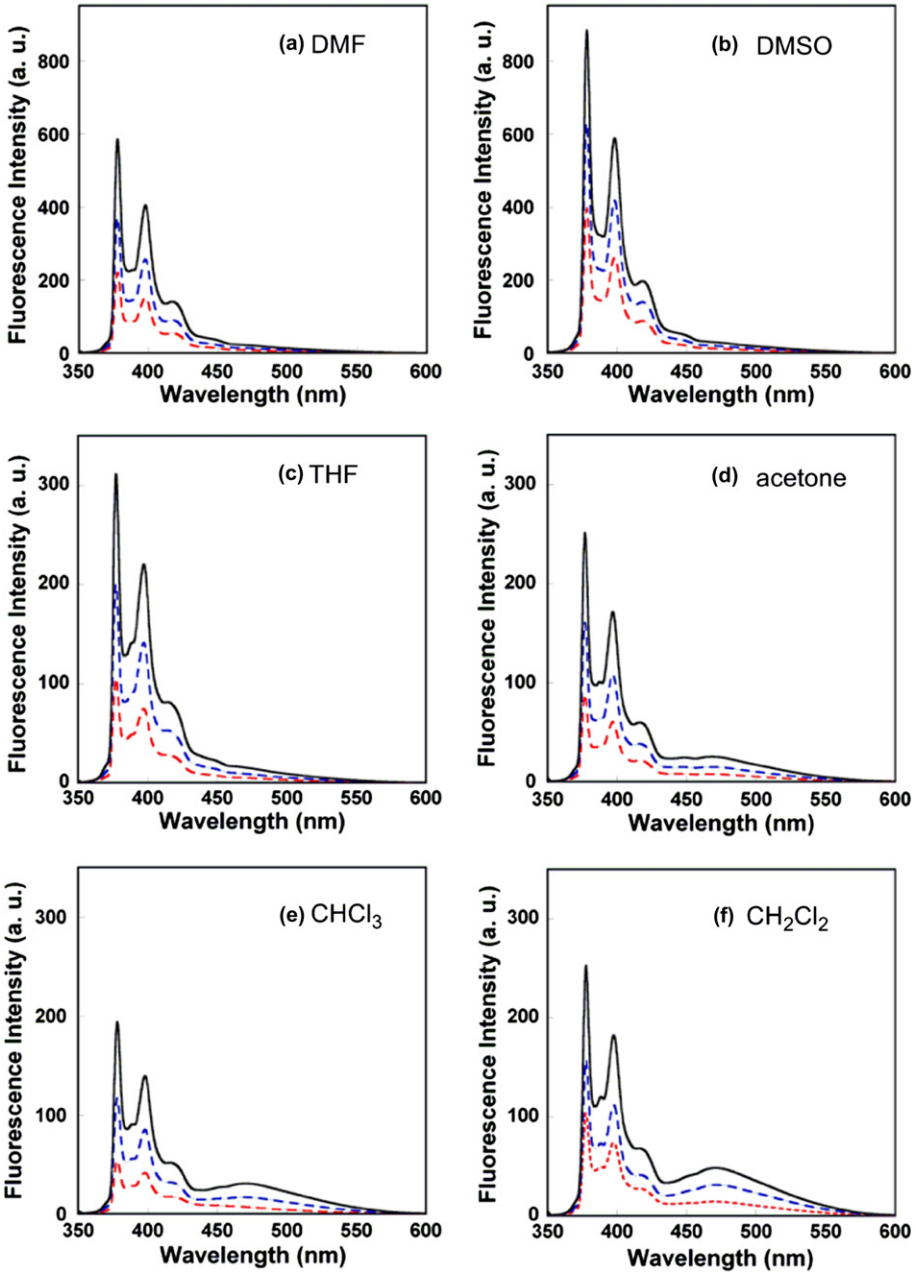


Fig. 5. Fluorescence spectra of compound **4** [5 (black line), 2.5 (blue dashed line), and 1.25 (red dashed line) μM] in various solvents at 293 K (λ_{ex}: 345 nm).

in which its major conformer was determined to be the trans form by NMR study. On the other hand, compound **4** emitted excimer fluorescence in less polar CH_2Cl_2 and $CHCl_3$, in which it existed predominantly as the cis conformer. Excimer fluorescence was observed at an intermediate level in acetone, in which the ratio of cis to trans conformer was 1:1 as determined from NMR study. Thus, excimer fluorescence of compound **4** was increased under conditions of cis conformational preference, which indicates that the introduction of the two pyrene units makes it possible to sense the solvent-dependent conformational change of *N*-phenylbenzohydroxamic acid in terms of fluorescence change.

The solvent-dependent fluorescence property of compound **4** resulted from the change of the ratio of cis and trans conformers in equilibrium. The energy barrier between the two conformers was 10.7 kcal/mol in acetone-d_6, as determined by temperature-dependent ^{1}H NMR study. Typical molecular switches must have a sufficiently high energy barrier to allow two switchable states to be distinguished, but the present model shows that an equilibrium change with a relatively low energy barrier can be employed for switching in an appropriate scaffold.

In our previous studies on an *N*-methylbenzanilide derivative with two pyrene units (**2b**), the ratio of excimer fluorescence (at 470 nm) to monomer fluorescence (at 398 nm) in CH_2Cl_2 was 0.74. A much higher ratio (3.67) was observed with the (*cis*,*cis*) folded *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea structure bearing two pyrenes at the *para* position on each aryl ring via ethylene linkers.[10] Compared with these *N*-methylated amide and urea compounds, the excimer fluorescence of compound **4** was not so marked, and its monomer fluorescence was still moderate even in CH_2Cl_2 and $CHCl_3$, in which only the cis conformer was detected by NMR study. The difference presumably arises from the folded structure of the cis conformers. In the crystal structures, the dihedral angle between the two phenyl rings is 70° for the conformer of *N*-phenylbenzohydroxamic acid (**3**), while it is 60° for *N*-methylbenzanilide (**2a**), and 35° for *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea.[13] Thus, a smaller dihedral angle between the two phenyl rings permits better orientation of the two pyrene moieties for intramolecular excimer formation. By optimization of the linker group between *N*-phenylbenzohydroxamic acid and the two pyrene units, and those substituent sites, it may be possible to develop fluorescent derivatives of *N*-phenylbenzohydroxamic acid with larger solvent-dependent fluorescence change, and such molecule could be a good candidate as a fluorescent sensor of solvent property.

4. Conclusion

In conclusion, we designed and synthesized the *N*-phenylbenzohydroxamic acid derivative (**4**), bearing two pyrene molecules on the phenyl rings via ethylene linkers, and showed that the solvent-dependent conformational alteration of the *N*-phenylbenzohydroxamic acid moiety is reflected in a moderate change of the fluorescence properties. These results demonstrate that the structural characteristics of *N*-hydroxybenzanilide can be applied as a core structure of fluorescent sensor for solvent property. To date, several types of aromatic amides, which exhibit conformational change in response to various types of environmental change such as pH and redox state, have been reported.[14] By utilizing the similar strategy shown in this paper, they could be transformed to fluorescent sensors for various environmental conditions, and such work is in progress.

5. Experimental section

5.1. Synthesis of compound 6

A mixture of 1-bromopyrene (**5**, 301 mg, 1.07 mmol), trimethylsilylacetylene (1.4 ml, 2.0 mmol), $PdCl_2(PPh_3)_2$ (45 mg, 0.064 mmol), and triethylamine (30 ml) was heated at 70 °C in a sealed tube under argon for 23 h. After evaporation, the residue was purified by silica gel column chromatography (eluent: *n*-hexane) to afford **6** (316 mg, 1.06 mmol, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.57 (1H, d, J=8.8 Hz), 8.12 (8H, m), 0.39 (9H, s).

5.2. Synthesis of compound 7

Potassium fluoride (74 mg, 1.27 mmol) was added to a solution of **6** (102 mg, 0.34 mmol) in THF (23 ml) and methanol (23 ml). The reaction mixture was stirred at room temperature for 65 h. After evaporation, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate=8:1) to afford **7** (44 mg, 0.19 mmol, 57%) as brown powder. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.58 (1H, d, J=9.1 Hz), 8.21 (1H, d, J=7.6 Hz), 8.18 (1H, d, J=8.6 Hz), 8.17 (1H, d, J=8.0 Hz), 8.16 (1H, d, J=9.1 Hz), 8.08 (1H, d, J=7.9 Hz), 8.08 (1H, d, J=8.9 Hz), 8.02 (1H, t, J=7.6 Hz), 8.01 (1H, d, J=8.9 Hz) , 3.65 (1H, s); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 132.6, 131.7, 131.3, 131.1, 130.3, 128.7, 128.5, 127.3, 126.4, 125.8, 125.8, 125.4, 124.5, 124.4, 124.3, 116.6, 82.9, 82.7.

5.3. Synthesis of compound 9

One drop of DMF was added to a solution of 4-iodobenzoic acid (**8**, 228 mg, 0.92 mmol) in thionyl chloride (4 ml). The reaction mixture was stirred at room temperature for 3.5 h, then evaporated. The residue was taken up in anhydrous toluene (10 ml) and again evaporated. The resultant residue was dissolved in anhydrous pyridine (3 ml). A solution of 4-iodophenylhydroxylamine (184 mg, 0.78 mmol) in anhydrous toluene (7 ml) was added to the above solution, and the reaction mixture was stirred at room temperature for 12 h. Methanol and water were added, and the whole was extracted with ethyl acetate. The organic layer was washed with 2 M hydrochloric acid, and brine, dried over $MgSO_4$, and evaporated. The residue was suspended in CH_2Cl_2 and collected by filtration to give **9** (204 mg, 0.44 mmol, 56%). Pale brown plates (AcOEt); mp 197.8–200.9 °C (dec); ^{1}H NMR (THF-d_8, 600 MHz) δ 9.72 (1H, s), 7.77 (2H, d, J=8.4 Hz), 7.67 (2H, d, J=8.9 Hz), 7.49 (2H, d, J=8.7 Hz), 7.46 (2H, d, J=8.3 Hz); ^{13}C NMR (THF-d_8, 150 MHz) δ 168.1, 143.2, 138.5, 138.0, 136.2, 131.6, 123.6, 97.8, 89.5; HRMS (ESI$^+$) calcd for $C_{13}H_{10}I_2NO_2$ (M+H$^+$): 465.8795; found: 465.8804; IR 3161.7, 1606.4, 1583.3 cm^{-1}.

5.4. Synthesis of compound 10

3,4-Dihydro-2*H*-pyran (0.09 ml) was added to a mixture of *p*-toluenesulfonic acid monohydrate (8 mg, 0.04 mmol) and **9** (204 mg, 0.44 mmol) in CH_2Cl_2 (40 ml) under an Ar atmosphere, and the mixture was stirred for 4 h at room temperature. The mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (eluent: acetone/methylene chloride=1:40) to afford **10** (211 mg, 0.38 mmol, 88%). Colorless needles (AcOEt); mp 157.2–157.9 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.66 (4H, m), 7.30 (2H, d, J=8.3 Hz), 7.18 (2H, d, J=8.6 Hz), 5.10 (1H, s), 3.39 (2H, m), 1.70 (3H, m), 1.54 (2H, m), 1.46 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 167.8, 140.9, 138.3, 137.4, 133.9, 130.6, 128.0, 102.6, 97.7, 92.9, 62.7, 28.4, 24.9, 18.5; HRMS (ESI$^+$) calcd for $C_{18}H_{17}I_2NNaO_3$ (M+Na$^+$): 571.9190; found: 571.9180; IR 1681.6, 1582.3 cm^{-1}.

5.5. Synthesis of compound 11

A solution of **7** (117 mg, 0.52 mmol) in triethylamine (4.5 ml) and THF (2 ml) was added to a mixture of **10** (94 mg, 0.17 mmol), $PdCl_2(PPh_3)_2$ (25 mg, 0.036 mmol), and CuI (14 mg, 0.072 mmol) in triethylamine (2 ml) and THF (2.5 ml) at 65 °C under an Ar

atmosphere. The reaction mixture was stirred at 65 °C for 3 h. After evaporation, the residue was purified by silica gel column chromatography (eluent: methylene chloride) to afford **11** (112 mg, 0.15 mmol, 87%) as brownish oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.64 (1H, d, J=9.1 Hz), 8.63 (1H, d, J=9.1 Hz), 8.22 (2H, d, J=7.6 Hz), 8.20 (2H, d, J=7.9 Hz), 8.19 (2H, d, J=8.0 Hz), 8.18 (2H, d, J=9.1 Hz), 8.13 (2H, dd, J=7.9, 1.3 Hz), 8.10 (2H, dd, J=8.9, 1.3 Hz), 8.05 (2H, d, J=8.1 Hz), 8.03 (2H, t, J=7.5 Hz), 7.72 (2H, d, J=8.5 Hz), 7.70 (4H, d, J=9.1 Hz), 7.55 (2H, d, J=8.4 Hz), 5.29 (1H, br), 3.58 (1H, m), 3.48 (1H, m), 1.89 (1H, m), 1.80 (2H, m),1.63 (1H, m), 1.55 (2H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 168.0, 141.2, 134.3, 132.5, 132.2, 132.1, 131.7, 131.6, 131.4, 131.2, 131.2, 129.9, 129.8, 129.3, 128.7, 128.6, 128.5, 128.5, 127.4, 126.5, 126.4, 126.3, 126.2, 125.9, 125.9, 125.8, 125.6, 125.5, 124.7, 124.7, 124.6, 124.5, 124.4, 122.9, 117.5, 117.3, 102.7, 94.5, 94.5, 91.0, 90.0, 62.8, 28.5, 25.1, 18.6; HRMS (ESI$^+$) calcd for $C_{54}H_{36}NO_3$ (M+H$^+$): 746.2690; found: 746.2696; IR: 1654.6, 1623.8, 1601.6, 1583.3 cm^{-1}.

5.6. Synthesis of compound 12

Palladium hydroxide on carbon (88 mg) was added to a solution of **11** (204 mg, 0.27 mmol) in ethyl acetate (22 ml) at room temperature under an Ar atmosphere. The reaction mixture was stirred for 3 h under a hydrogen atmosphere. After filtration, the residue was dissolved with CH_2Cl_2 and water. The organic layer was washed with brine, dried with $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (eluent: methylene chloride, then n-hexane/ethyl acetate=5:2) to afford **12** (106 mg, 0.14 mmol, 52%). Yellow powder; mp 191.8–204.2 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.25 (2H, d, J=9.3 Hz), 8.16 (2H, d, J=7.9 Hz), 8.15 (2H, d, J=8.0 Hz), 8.09 (2H, d, J=9.2 Hz), 8.03 (1H, d, J=7.7 Hz), 8.03 (1H, d, J=7.7 Hz), 8.00 (4H, m), 7.98 (2H, t, J=7.6 Hz), 7.69 (2H, d, J=7.7 Hz), 7.47 (2H, d, J=8.0 Hz), 7.29 (2H, d, J=8.2 Hz), 7.10 (2H, d, J=7.6 Hz), 7.09 (2H, d, J=7.7 Hz), 5.26 (1H, s), 3.59 (4H, m), 3.56 (1H, m), 3.40 (1H, m), 3.12 (4H, m), 1.84 (1H, m), 1.75 (2H, m), 1.58 (2H, m), 1.45 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 168.6, 144.5, 141.4, 139.8, 135.5, 135.4, 132.5, 131.5, 131.0, 131.0, 130.1, 130.1, 129.3, 129.3, 129.2, 129.2, 128.7, 128.7, 128.4, 128.2, 127.6, 127.6, 127.6, 127.5, 127.5, 127.3, 126.9, 126.0, 125.2, 125.1, 124.9, 124.8, 124.8, 123.2, 123.2, 102.0, 62.4, 37.9, 37.6, 35.3, 35.3, 28.5, 25.2, 18.5; HRMS (ESI$^+$) calcd for $C_{54}H_{43}NNaO_3$ (M+Na$^+$): 776.3135; found: 776.3164; IR: 1646.0, 1603.5 cm^{-1}.

5.7. Synthesis of compound 4

A mixture of **12** (54 mg, 0.07 mmol) and p-toluenesulfonic acid monohydrate (38 mg, 0.20 mmol) in methanol (5 ml) and methylene chloride (5 ml) was stirred for 5 h at room temperature. After evaporation, the residue was suspended with methanol and filtered to give **4** (42 mg, 0.062 mmol, 89%). Yellow plates (acetone); mp 210.3–211.2 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.10 (1H, s), 8.23 (1H, d, J=9.2 Hz), 8.20 (1H, d, J=9.2 Hz), 8.17 (1H, d, J=7.5 Hz), 8.16 (1H, d, J=7.4 Hz), 8.13 (2H, d, J=7.6 Hz), 8.09 (1H, d, J=9.2 Hz), 8.07 (1H, d, J=9.2 Hz), 8.04 (2H, d, J=7.8 Hz), 8.00 (4H, m), 7.97 (2H, t, J=7.6 Hz), 7.68 (2H, d, J=7.8 Hz), 7.29 (2H, d, J=8.2 Hz), 7.05 (2H, d, J=8.5 Hz), 7.01 (2H, d, J=8.3 Hz), 7.00 (2H, d, J=8.2 Hz), 3.58 (4H, t, J=7.8 Hz), 3.11 (4H, m); ^{13}C NMR (THF-d_8, 150 MHz) δ 167.9, 145.5, 141.7, 140.4, 137.1, 137.0, 134.4, 132.8, 132.3, 131.4, 131.3, 130.3, 129.9, 129.6, 128.9, 128.6, 128.6, 128.5, 128.5, 128.4, 127.8, 127.7, 126.9, 126.9, 126.3, 126.3, 126.3, 126.0, 126.0, 125.9, 125.9, 125.9, 125.8, 124.4, 124.4, 123.6, 39.0, 38.7, 36.6, 36.3; HRMS (ESI$^+$) calcd for $C_{49}H_{35}NNaO_2$ (M+Na$^+$): 692.2560; found: 692.2587; IR: 3131.8, 3046.0, 1603.5, 1588.1, 1565.0 cm^{-1}.

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Supplementary data

Temperature-dependent ^{1}H NMR spectra of compound **4** in various solvents, The fluorescence spectra of compound **13** in various solvents, and ^{1}H and ^{13}C NMR data of synthetic intermediates. Supplementary data related to this article can be found in the online version, at doi:10.1016/j.tet.2012.02.012.

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