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Advance Publication on the web January 16, 2020 doi:10.1246/cl.190924

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# Naked Eye Detection of Anions by 2,2'-Bianthracene Derivative Bearing Urea Groups in Various Organic Solvents

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A highly fluorescent 2,2'-bianthryl derivative 1 bearing urea groups (2) was prepared as an anion receptor. The UV-vis and fluorescence titrations of 2 in various organic 2 3 4 solvents revealed that the association constants  $(K_{11})$  were 5 correlated with acceptor number and Swain acity of the solvents used, and tetrahydrofuran was found to strongly 6 enhance the  $K_{11}$  for Cl<sup>-</sup> and AcO<sup>-</sup> due to enthalpy driven 8 complexation, in which naked eye detection of AcO<sup>-</sup> was 9 achieved.

## 10 Keywords: Anion recognition, Naked eye anion sensing,11 2,2'-Bianthryl anion receptor

12 Anions are ubiquitous and play a wide variety of roles 13 in chemical, biological, environmental, and industrial fields.<sup>1-3</sup> The importance of the anions have motivated 14 15 supramolecular chemists to develop a variety of receptors to 16 bind and sense the anionic species. For achieving high binding affinity and selectivity for the anion, hydrogen bond 17 18 donor (HBD) group such as urea, amide, and pyrrole have 19 widely been employed as a recognition site of the receptors 20 because of its directionality making the recognition site 21 complementary to various geometries of the anion.<sup>2-6</sup>

22 Among anion sensing techniques, naked eye anion 23 detection by fluorimetry and colorimetry are quite useful due 24 to their affordability and ease of use.<sup>7</sup> Although many naked 25 eye anion sensors have been reported, the naked eye detection 26 by a hydrogen-bond based receptor has been less explored, in 27 which the most of the receptors with HBD group show the 28 selectivity only for the relatively highly basic anions such as 29 F<sup>-</sup> and AcO<sup>-</sup> with deprotonation of the acidic HDB group.<sup>8-</sup> 12 30

31 In our group, a 2,2'-binaphthalene-based receptor (1, 32 Figure 1) having high 1: 1 binding constants  $(K_{11})$  for AcO<sup>-</sup> 33 and Cl<sup>-</sup> in acetonitrile by cooperative hydrogen bonds with 34 urea groups has been reported.13 However, the naked eye 35 detection with 1 has not yet been achieved due to the fluorescence emission at short wavelength despite the 36 37 observation of fluorescent quenching of 1 by the addition of 38 AcO<sup>-.13</sup> We have described naked eye detection of Ba<sup>2+</sup> with 39 a 2,2'-bianthracene bearing aza-15-crown-5 moieties by expanding the  $\pi$ -conjugation of 2,2'-banaphthalene.<sup>14,15</sup> 40



Figure 1. Chemical structures of 1 and 3.

41 Taking this into account, the naked eye anion detection is 42 expected to be achieved by using a bisureido 2,2'-bianthryl 43 receptor (2, Scheme 1) with longer  $\pi$ -conjugate system than 44 1. Thus, in this study, we prepared 2 to study the anion recognition ability and fluorescent change upon the 45 recognition in various solvents by UV-vis and fluorescent 46 47 titrations. In addition, we explored the solvent effect on the 48  $K_{11}$  of **2** and the complexation mechanism depending on the 49 solvent used from the thermodynamic parameters during the 50 complexations. While there have been the studies relating to 51 the solvent effect on the hydrogen-bonding-anion recognition 52 in mixed solvent or in limited solvents,<sup>16-24</sup> the effect of a 53 wide range of solvents have been studied only for a shape-54 persistent triazolophane macrocycle and a bambusuril macrocycle.<sup>25,26</sup> Furthermore, the results of these studies 55 56 describing the correlation between the binding affinity with 57 TBACl and different solvent parameters including reciprocal 58 of the dielectric constant<sup>25</sup> and Swain acity<sup>26</sup> show that the 59 solvent effect on the hydrogen-binding anion recognition 60 would be affected by the structure of the receptor. Through 61 the explorations with a wide variety of solvents, we show the 62 anion binding affinity of the relatively flexible acyclic 63 receptor also inversely correlate with the acidity of the 64 solvents as is the case with bambusuril macrocycle.<sup>26</sup>

65 8,8'-Di(3-tert-butylureido)-2,2'-binaphthalene (1) was synthesized according to the procedure we have previously 66 reported.<sup>13,27</sup> 1-(3-t-Butylureido)naphthalene (3, Figure 1) 67 68 was synthesized by reaction of t-butylamine with the 69 isocyanate<sup>28</sup> prepared from 1-naphthylamine using triphosgene. Synthesis of 9,9'-di(3-t-butylureido)-2,2'-70 bianthracene (2) was summarized in Scheme 1. 2-71 72 Bromoanthracene, which was prepared from bromobenzene according to the literatures,<sup>29-32</sup> was reacted with nitric acid 73



Scheme 1. Synthesis of 2. (a) HNO<sub>3</sub>, AcOH, 50 °C. (b) HCl, rt. (c) NaOH<sub>aq</sub>, 60 °C. (d) Fe, NH<sub>4</sub>Cl, acetone / H<sub>2</sub>O, reflux.
(e) Zn, PPh<sub>3</sub>, Bpy, NiCl<sub>2</sub>, DMAc, 60 °C. (f) Triphosgene, *i*Pr<sub>2</sub>EtN, THF, rt. (g) *t*-Butylamine, THF, 50 °C.

to afford 2-bromo-9- and 2-bromo-10-nitoroanthracene, 1 2 respectively in 1.00:0.59 ratio from the <sup>1</sup>H NMR.<sup>33</sup> 3 Recrystallization of the mixture from mixed solvent (CHCl3: 4 Hexane = 1: 1) afforded yellow needle crystals which was 5 identified to be desired 2-bromo-9-nitoroanthracene (4) by Xray diffraction with the single-crystals grown by vaper 6 7 diffusion of hexane into a solution of 4 in CHCl<sub>3</sub> (Figure S28).<sup>34</sup> Reduction of **4** with iron and ammonium chloride,<sup>35</sup> 8 followed by homocoupling with Ni catalyst gave 9,9'-9 diamino-2,2'-bianthracene (6).<sup>27,36,37</sup> The product was treated 10 with triphosgene, and the produced isocyanate was reacted 11 with tert-butylamine to obtain bisureido 2,2'-bianthracene 12  $(2)^{13}$  and the product was identified with NMR (<sup>1</sup>H, <sup>13</sup>C, 13 14 COSY, HMBC, and HMQC) and HRMS.

15 Although the originally reported 2,2'-binaphthalene 16 having *n*-butyl groups<sup>27,37</sup> shows high binding affinity for Cl<sup>-</sup>, 17 the low solubility in organic solvents is troublesome. The 18 solubility was improved by substitution by *t*-butyl groups 19 (1).<sup>13</sup> Hence, we evaluated the solubility of 2 by means of the 20 same evaluation method as 1. The saturated concentration of 21 2 in DMSO was found to be 25-40 times greater than that in MeCN, THF, and CHCl<sub>3</sub> (Table 1). The saturated 22 concentration of 2 in DMSO (7.67×10<sup>-3</sup> mol dm<sup>-3</sup>) was 23 approximately a half of  $1 (16 \times 10^{-3} \text{ mol dm}^{-3})$ . Although this 24 25 lower saturated concentration would be due to more 26 favorable  $\pi$ - $\pi$  stacking of 2 having longer  $\pi$ -conjugated 27 system than 1, the concentration is sufficient to use 2 as an 28 optical sensor with UV-vis and fluorescent titrations, in 29 which concentration of  $\sim 10^{-5}$  mol dm<sup>-3</sup> is usually required.

30

31 **Table 1**. Saturated concentrations of **1** and **2** in various 32 solvents.

Solvent	Saturated concentration / mol dm <sup>-3</sup>			
-	<b>1</b> <sup>a</sup>	2		
CHCl <sub>3</sub>	3.1×10 <sup>-4</sup>	$2.71 \times 10^{-4}$		
THF	2.43×10 <sup>-3</sup>	$2.90 \times 10^{-4}$		
MeCN	$8.0 \times 10^{-5}$	$1.95 \times 10^{-4}$		
DMSO	16.0×10 <sup>-3</sup>	$7.67 \times 10^{-3}$		

<sup>33 &</sup>lt;sup>a</sup> 34

35 UV-vis spectrum of 2 shows characteristic absorbance 36 at 408 and 385 nm, which is significantly longer than the 37 corresponding 1 (Figure S1). Considering a report by Wang and Wu<sup>38</sup> that HOMO-LUMO energy gap of 2,2'-38 bianthracene calculated by density functional theory (DFT) 39 40 at B3LYP/6-31G(d) level is 3.230 eV (384 nm), absorption 41 around 400 nm of 2 would be derived from absorption 42 between the HOMO and LUMO ( $\pi$ - $\pi$ \* transition). UV-vis 43 titrations of 1 have been performed in MeCN at 298 K in our group,  $^{13}$  therefore, the titrations of **2** was also carried out in 44 the same condition. Upon the addition of TBACl (~50 eq), 45 hyperchromic and hypochromic shift of 2 around 440 nm and 46 47 400 nm via isosbestic points at 424, 338-330, 304, 287.5, and 48 259.5 nm were observed (Figure 2). Nonlinear curve fitting 49 analysis of the titration with 1:1 complex model showed good 50 agreement between the absorbance change and the theorical 51 curve, which suggests the 1:1 complex formation. 52 Furthermore, the calculated  $K_{11}$  (1.3×10<sup>4</sup> mol<sup>-1</sup> dm<sup>3</sup>) was

53 found to be 61 times smaller than that of 1  $(7.9 \times 10^5 \text{ mol}^{-1})$ 54 dm<sup>3</sup>, Table S1). To reveal further insight into the difference 55 of the  $K_{11}$  for Cl<sup>-</sup> between 2 and 1, the optimized structures 56 of the complexes were calculated by DFT at B3LYP/6-57 31+G(d) level. While the dihedral angle of C9a-C9-N1-H of 58 the optimized 2•Cl<sup>-</sup> was 41°, the corresponding one of C8a-59 C8-N1-H of the optimized 1•Cl<sup>-</sup> was 21° (Figure S16). 60 Receptor 2 would adopt the larger dihedral angle to prevent 61 the steric repulsion of C8-H of the anthryl moiety with the carbonyl oxygen of the urea, which would lead to the 62 decrease in the  $K_{11}$  with decreasing acidity of the urea 63 hydrogens due to less overlapping p-orbitals of the anthryl 64 and the urea groups of 2. As is the case with Cl-, similar 65 hyperchromic and hypochromic effect were observed for 2 66 upon the addition of AcO<sup>-</sup>. Moreover, a trend of  $K_{11}$  for AcO<sup>-</sup> 67 68 was similar to that for Cl<sup>-</sup>; that is, the  $K_{11}$  of **2** for AcO<sup>-</sup> in 69 MeCN ( $2.8 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ ) was 72 times smaller than that of 70 1 (2.0×  $10^6 \text{ mol}^{-1} \text{ dm}^3$ ).

UV-vis titrations of 2 in various solvents such as THF,
AcOEt, acetone, benzene, 1,4-dioxane, CH<sub>2</sub>Cl<sub>2</sub>, DMF, CHCl<sub>3</sub>,



**Figure 2.** (a) UV-vis spectral changes of **2** upon the addition of 0–50 eq of TBACl in MeCN containing 1% DMSO at 298 K. [**2**] =  $1.01 \times 10^{-5}$  mol dm<sup>-3</sup>. (b) Absorbance changes at 410 nm. A theorical 1: 1 binding isotherm indicates as a solid curve.

73 and DMSO were also performed at 298 K using TBACl as a

- 74 guest (Figure S6) for evaluating solvent effect on the anion
- 75 recognition. As is the case in the titrations in MeCN, 1: 1
- 76 complex formation of 2 with Cl<sup>-</sup> was confirmed in any

1 solvents by the nonlinear curve fitting analysis, and their  $K_{11}$ 2 were summarized in Table S1. Among them, the  $K_{11}$  in THF

2 were summarized in Table S1. Among them, the  $K_{11}$  in THF 3 (4.4×10<sup>6</sup> mol<sup>-1</sup> dm<sup>3</sup>) was the largest and 338 times greater

4 than that in MeCN. Furthermore, the  $K_{11}$  of **2** for Cl<sup>-</sup> in THF

5  $(4.4 \times 10^6 \text{ mol}^{-1} \text{ dm}^3)$  was 5.6 times greater than that of 1 in

6 MeCN, which suggests strong solvent effect on the anion 7 recognition. In addition, the  $K_{11}$  of **2** for AcO<sup>-</sup> was also the 8 greatest in THF.

9 In order to confirm whether the enhancement of the  $K_{11}$ 10 by THF is unique to 2, UV-vis titrations of 1 and 3 with TBACl in MeCN or THF at 298 K were also performed 11 (Figure S2 and S4). Both receptors were found to form the 12 1:1 complex in MeCN and THF, and their  $K_{11}$  for Cl<sup>-</sup> were 13 14 enhanced in THF. This indicates the enhancement of  $K_{11}$  for 15 Cl<sup>-</sup> by THF is general for such urea based receptors. While 16 the  $K_{11}$  of **3** for Cl<sup>-</sup> in THF (7.5 × 10<sup>3</sup> mol<sup>-1</sup> dm<sup>3</sup>) was 21 times 17 larger than that in MeCN, 1 and 2 showed more than 400 and 18 338 times larger binding affinity, respectively. Hence, in 19 addition to the solvation effect, donation of cooperative 20 hydrogen bonds by the bisurea group seems to be necessary 21 to strongly enhance the  $K_{11}$  of the receptors. The  $K_{11}$  of the 22 above receptors for AcO<sup>-</sup> were also found to be enhanced by 23 THF and the cooperative hydrogen bond donation.

24 When the  $K_{11}$  of **2** for Cl<sup>-</sup> in MeCN and THF was 25 compared to that in other solvents, the  $K_{11}$  became small in 26 order of THF > AcOEt > acetone > benzene > 1,4-dioxane > 27  $CH_2Cl_2 > MeCN > DMF > CHCl_3 > DMSO$  (Table S1). 28 Furthermore, plotting of these  $K_{11}$  against solvent factors 29 including relative permittivity  $(\varepsilon_r)$ , solvent orientation 30 polarizability ( $\Delta f$ ), Dimroth-Reichardt parameter ( $E_T^N$ ), 31 Gutmann donor number  $(DN^{N})$ , acceptor number (AN), and 32 Swain acity suggests that the  $K_{11}$  of **2** for Cl<sup>-</sup> had the highest 33 correlation with AN and Swain acity, and the  $K_{11}$  increased 34 with decreasing these parameters (Figure 3 and Figure S12). 35 Although the order of the  $K_{11}$  for AcO<sup>-</sup> was slightly different 36 form that for Cl<sup>-</sup>, the binding affinity for AcO<sup>-</sup> also had the 37 highest correlation with the same parameters (Figure S13).

38 *AN* and Swain acity are the solvent parameters which 39 can quantify the acidity of the solvent,<sup>39,40</sup> thus, the anion with 40 higher basicity than electron neutral **2** would be more 41 profoundly affected by these parameters. Considering an



**Figure 3.** Relationship of log  $K_{11}$  of **2** with Cl<sup>-</sup> *vs* AN of solvents used.

42 increase in the  $K_{11}$  for Cl<sup>-</sup> and AcO<sup>-</sup> with decreasing the 43 acidity of the solvents, free anions would be weakly solvated 44 in the solvent with smaller acidity, which would lead to less 45 competition between the solvation and the complexation of 46 the anion. Hence, the complexation would be more favorable 47 in the solvent with smaller acidity such as THF.

48 To explore the anion selectivity of 2, UV-vis titrations 49 of 2 in THF at 298 K were performed using TBA salts of Br-, 50 NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. From the results of the nonlinear 51 curve fitting analysis of the spectral changes, 1:1 complex 52 formation of 2 with any anions was indicated and the 53 calculated  $K_{11}$  was found to be in the order of  $Cl^- > AcO^- \approx$ 54  $H_2PO_4^- > Br^- > HSO_4^- > NO_3^-$  (Figure S8 and Table 2) as 55 observed for 2,2'-binaphthalene having *n*-butyl groups.<sup>11</sup> 56

57 Table 2. The association constants of 2 for various TBA salts
58 of anions in THF containing 1% DMSO obtained from UV59 vis titrations at 298 K.

Anion	$K_{11}$ a
NO <sub>3</sub> <sup>-</sup>	$(1.07\pm 0.07)  imes 10^4$
$\mathrm{HSO}_{4}^{-}$	$(1.73 \pm 0.02)  imes 10^4$
$\mathrm{Br}^-$	$(3.84 \pm 0.29) \times 10^5$
$AcO^{-}$	$(1.61 \pm 0.04) \times 10^{6}$
$H_2PO_4^-$	$(1.67\pm 0.02)  imes 10^{6}$
Cl <sup>-</sup>	$(4.40\pm 0.14) imes 10^{6}$

60  $a[2] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}.$ 

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62 Thermodynamic parameters during the complexation of 63 2 with Cl<sup>-</sup> and AcO<sup>-</sup> measured by van't Hoff analysis of UV-64 vis titrations in MeCN or THF at various temperatures (290-65 322 K) should give further information on the solvent 66 effect.<sup>41</sup> The complexations of **2** with Cl<sup>-</sup> and AcO<sup>-</sup> were 67 found to be entropically less favorable ( $T\Delta S < 0$ ) but 68 enthalpically much favorable ( $\Delta H > 0$ ) in THF than those in 69 MeCN (Table 3). As mentioned above, the anion in THF 70 would be weakly solvated, then enthalpy driven 71 complexation was observed.

73 Table 3. Thermodynamic parameters of complexation
74 between 2 and anions in MeCN and THF containing 1%
75 DMSO obtained from UV-vis titrations.

	Anion	Solvent	$\Delta G$	$\Delta H$	$T\Delta S^{a}$
			kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>
	Cl <sup>-</sup>	MeCN	-23.51	-19.48	4.04
	$Cl^-$	THF	-37.91	-41.47	-3.57
	$AcO^{-}$	MeCN	-25.19	-23.41	1.77
	$AcO^{-}$	THF	-35.54	-41.83	-6.29
5	<sup>a</sup> at 298 K.				

76 °at 2 77

1 2 shows characteristic yellow-green fluorescence at 2 around 520 nm excited at 335 nm (the isosbestic point in the UV-vis titrations) in MeCN containing 1% DMSO originated 3 from the 2,2'-bianthryl moiety with 80 nm longer  $\pi$ -4 5 conjugated system than 2,2'-binaphthyl<sup>13</sup> as shown in Figure S9. The  $\lambda_{Fl,max}$  of **2** was shifted to longer wavelength and the 6 7 enhancement of the fluorescent intensity via an isoemissive 8 point at 480 nm was observed upon the addition of ~70 eq of 9 TBACl. As is the case in UV-vis titrations, 1: 1 complex 10 formation of 2 with Cl<sup>-</sup> was confirmed by the nonlinear curve fitting analysis of fluorescent changes at 520 nm. Contrary to 11 this, significant decrease in fluorescent intensity was 12 observed for 2 upon the addition of TBAAcO (Figure S10). 13 14 The calculated  $K_{11}$  of **2** for Cl<sup>-</sup> and AcO<sup>-</sup> were almost 15 identical to those obtained by UV-vis titrations.

16 The fluorescent titrations of 2 in other solvents were 17 also performed at 298 K. In the absence of any anions, the 18  $\lambda_{\text{Fl.max}}$  of **2** in each solvent were different from that in MeCN. 19 For example, the  $\lambda_{Fl,max}$  in THF (511 nm) was 9 nm shorter 20 than that in MeCN (Figure S9) due to smaller ICT characters in less polar solvent.42 21

22 The fluorescence intensities of 2 in the solvents other 23 than MeCN were also changed by the addition of TBACl (Figure S9). Among them, the increasing in the 24 25 fluorescence intensities of 2 was observed in relatively 26 polar solvents such as MeCN, acetone, DMF, and 27 DMSO, while the intensities decreased in other solvents upon the addition of Cl<sup>-</sup>. For more detail of the 28 29 mechanism, further studies are required in the future 30 work. The association constants determined from 31 fluorescence titrations in such solvents were fairly good 32 agreement to those obtained by UV-vis titrations, and the  $K_{11}$ 33 in THF was the highest among all other solvents. Moreover, 34 the decrease of fluorescence intensity by AcO<sup>-</sup> in THF was 35 clearly checked with naked-eye (Figure 4, 5, and S14). Other 36 anions such as Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> were also 37 employed in the fluorescence titrations of 2 in THF at 298 K, 38 and the  $K_{11}$  for these anions and fluorescence intensity 39 changes were smaller (Figure S11 and Table S2). Therefore, 40 2 would be utilized as a naked-eye sensor for the acetate.



Figure 4. Fluorescent spectral changes of 2 upon the addition of 0-6.0 eq of TBAAcO in THF containing1% DMSO at 298 K.  $[2] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ .  $\lambda_{ex} = 335 \text{ nm}$ .



Figure 5. Fluorescence of 2 in THF in the absence (a) or presence of 6 eq of TBAAcO (b).  $[2] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ .  $\lambda_{\rm ex} = 365$  nm.

41 In summary, bisurea based on 2,2'-bianthracene (2) was 42 successfully prepared and 2 had longer-wavelength 43 absorption than 1. Receptor 2 was sufficiently soluble in 44 DMSO. Although the  $K_{11}$  of **2** for Cl<sup>-</sup> was 61-fold smaller 45 than that of 1 due to a decrease in acidity of the urea protons 46 with increasing the dihedral angle between the urea and the 47 anthryl  $\pi$  surface, dramatically enhanced  $K_{11}$  of 2 was 48 observed in THF. The correlation of the  $K_{11}$  with AN and 49 Swain acity of the solvents and van't Hoff plots revealed that 50 enthalpy driven complexation by weakly solvated anions. 51 Moreover, significant fluorescent intensity changes of 2 by 52 the addition of TBAAcO indicates 2 can be utilized as a 53 naked-eye anionic sensor.

#### 55 Acknowledgement

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56 The authors would like to thank Professor Hiroshi Katagiri, 57 Mr. Yusuke Shibuya, and Mr. Amane Matsunaga, Yamagata 58 University for the measurements of single crystal X-ray 59 diffraction and HRMS.

61 Supporting Information is available on http://dx.doi.org/10.1246/cl.\*\*\*\*\*. 62

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