## Accepted Manuscript

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Please cite this article as: J. Otani, T. Kikuchi, S. Higashida, T. Harada, M. Matsumura, Synthesis and properties of azonaphtharylamide pigments having arylamidegroups at 2- and 7-positions, *Journal of Molecular Structure* (2014), doi: http://dx.doi.org/10.1016/j.molstruc.2014.12.011

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#### Synthesis and properties of azonaphtharylamide pigments having arylamide groups at

2- and 7-positions

Junji Otani,<sup>a, \*</sup> Takeshi Kikuchi,<sup>b</sup> Suguru Higashida,<sup>c</sup> Takashi Harada,<sup>a</sup> and Michio

#### **Matsumura**<sup>a</sup>

<sup>a</sup> Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama,

Toyonaka, Osaka 560-8531, Japan

<sup>b</sup> Department of Bioinformatics, College of Life Sciences, Ritsumeikan University, 1-1-1

Nojihigashi, Kusatsu, Shiga 525-8577, Japan

<sup>c</sup> Environmental and Materials Chemistry Course, Osaka Prefecture University College of

Technology, 26-12 Saiwai, Neyagawa, Osaka 572-8572, Japan

Keywords:

Azonaphtharylamide pigments, Chromophore system, Bathochromic shift, Hyperchromic

effect, Light fastness

Abstract

We studied two azonaphtharylamide pigments having arylamide groups at the 2- and

7-positions on the naphthol ring. Presence of the 7-substited amide group distinguishes the

pigments from conventional azonaphtharylamide pigments derived from

3-hydroxy-2-naphthoic acid. The 7-substituent caused a hyperchromic effect but did not produce bathochromic shift in the optical absorption spectra in solution compared with the corresponding 7-unsubstituted counterparts. Molecular geometry optimizations through semi-empirical MO calculations showed that extent of the chromophore systems in the pigments with and without the 7-substituent is nearly the same, which is consistent with absence of the bathochromic shift. The MO calculations also showed that the MOs localized in 7-substituents are involved in the electronic transitions in the longest wavelength bands of the pigments, which is responsible for the hyperchromic effect. The 7-substituted pigments exhibited better resistivity to light and heat than the 7-unsubstituted ones.

#### 1. Introduction

An important class of industrial azo pigments is synthesized using hydroxynaphthalene (βnaphthol) and its derivatives as a base for coupling components [1,2]. Of the derivatives, 3-hydroxy-2-naphthoic acid is one of the most important starting materials. The naphthalene ring of the naphthoic acid is a conjugated polyene and forms the central structure of the chromophore in the resultant pigments. The carboxylic acid at the 2-position has been utilized for the syntheses of a variety of coupling components through a simple amidation procedure.

Consequently, the industrially important subclasses of azo pigments, e.g.,

azonaphtharylamide-type and benzimidazolone-type pigments, have been developed [2]. If an additional carboxylic acid is introduced to the naphthalene ring, further development of new azo pigments becomes possible. We tried to synthesize coupling components having amide groups at the 2- and 7-positions of the naphthol to develop new azonaphtharylamide-type pigments. For this purpose, we opted 3-hydroxy-2,7-naphthalene dicarboxylic acid 1, as shown in Fig.1, as a starting compound. This compound enables introduction of the same or mutually different substituents at the 2- and 7-positions through double amidation, which will allow development of a new subclass of azo pigments. We expect that the substituent at the 7 position may impart functionality to the pigments and improve their technical performance. One of the authors (JO) engaged in development of some of the pigments synthesized from 1 [3,4]. Here, we report synthesis and fundamental properties of two kinds of new azo pigments which were synthesized from **1**. As the coupling component, we chose 3-hydroxy-N2,N7-diphenyl-naphthalene-2,7-dicarboxamide 2 (Fig. 1) because of its structural simplicity. Concerning the properties of the pigments, we investigated the effect of the 7-substituents upon the optical properties and chemical stabilities.

#### 2. Results and discussion

#### 2.1 Target materials and syntheses

Fig. 1 shows the chemical structures of two 7-substituted azonaphtharylamide pigments prepared from **1** via coupling component **2**, i.e.,

4-(2,5-dichlorophenyl)azo-3-hydroxy-N2,N7-diphenylnaphthalene-2,7-dicarboxamide 3a and
4-(2-methly-5-nitrophenyl)azo-3-hydroxy-N2,N7-diphenylnaphthalene-2,7-dicarboxamide 4a.
For comparison, the chemical structures of the conventional 7-unsubstituted counterparts, i.e.,
4-(2,5-dichlorophenyl)azo-3-hydroxy-N-phenylnaphthalene-2-carboxamide (C.I. Pigment
Red 2, 3b) and

4-(2-methyl-5-nitrophenyl)azo-3-hydroxy-N-phenylnaphthalene-2-carboxamide (C.I. Pigment Red 22, **4b**), are also shown. For easy comparison with **2**, the structures of **3a**, **3b**, **4a** and **4b** are depicted in the hydroxy-azo configurations, although they can take the keto-hydrazone configurations.

Conventional 7-unsubstituted azonaphtharylamide pigments are divided into two groups in terms of the number of the amide group [2]. Group 1 contains a single amide group derived from 2-carboxylic acid, and Group 2 contains one or more additional amide groups (and/or sulfonamide groups) attached to the diazo component and/or 2-phenylcarboxamide. The pigments having a 7-substituent like **3a** and **4a** are the members of neither Group 1 nor Group 2 by the above definition due to presence of a 7-subtituent. Consequently, if the pigments derived from **2** demonstrate any advantages from technological and/or industrial point of view over the conventional azonaphtharylamide pigments, those pigments will create another new

subclass of azo pigments.

Syntheses of coupling component **2** and pigments **3a** and **4a** are shown in Scheme 1. In the process, 3-hydroxy-2,7-naphthalene dicarboxylic acid **1** was allowed to react with phosphorus trichloride to give acid chloride **5**, which was then amidated with aniline **6** to afford **2**. This compound was allowed to react with aniline diazonium fluoroboric salt **7** to produce **3a** or **4a**. For the synthesis, fluoroboric salt **7** was used because it is chemically stable and convenient to handle compared with the conventional chloride and nitrate salts [**5**]. The crude pigments were heated in N,N-dimethylformamide at 120-130°C for 3 hours to promote crystal growth [6]. The pigments thus obtained were more insoluble than the counterparts (**3b** and **4b**) in both polar and nonpolar solvents. The pigments **3a** and **4a** in a powder state as obtained were yellowish and bluish red, respectively, resembling those of **3b** and **4b**.

#### 2.2 Crystallinity of 3a and 4a

Powder X-ray diffraction patterns of **3a** and **4a** are shown in Figs. 2 and 3, respectively, together with those of **3b** and **4b**. Although they were heat-processed for crystal growth as mentioned above, the diffraction bands of **3a** and **4a** are broader than those of **3b** and **4b**.

The sizes of the crystallites of **3a** and **4a** were estimated to be 14.8 and 8.8 nm,

respectively, using Scherrer equation from the half maxima of the diffraction peaks at around

 $2\theta$ = 27.5°. Similarly, the sizes of the crystallites of **3b** and **4b** were estimated to be 16.1 and

16.0 nm, respectively. These results may suggest that the 7-phenylcarboxamide substituent hindered the growth of the crystallites of **3a** and **4a**.

#### 2.3 UV-Vis absorption spectra of the pigments

Figs. 4 and 5 show UV-Vis optical absorption spectra of **3a** and **3b** and of **4a** and **4b**, respectively, in N-methylpyrrolidone. The four compounds exhibit two broad and almost structureless bands: one from 470 to 580 nm and the other from **350** to 400 nm. Tables 1 and 2 summarize wavelengths of the absorption maxima and molar extinction coefficients of **3a** and **4a**, respectively, together with those of **3b** and **4b**. A bathochromic shift was not observed between **3a** and **3b** or between **4a** and **4b**. A hyperchromic effect of **3a** and **4a** was, however, clearly observed, particularly in the shorter wavelength region. The absence of a bathochromic shift suggests that extent of the chromophore systems of **3a** and **4a** are comparable with those of **3b** and **4b**, respectively, and that there is little involvement of the 7-substituent in the chromophore systems. This is consistent with the similarity of color tones in the powder samples. The hyperchromic effect observed will be discussed later.

#### 2.4 MO calculations for molecular geometry and electron transition

It has been shown that azonaphtharylamide pigments tend to adopt a keto-hydrazone form in solution and crystalline states [6-8]. A study on 1-phenylazo-2-naphthols also showed that

the keto-hydrazone form is energetically more stable than the hydroxy-azo form based on results of crystal structure analyses and DFT calculations [9]. Therefore, we optimized the molecular geometry of **3a** and **4a** with a keto-hydrazone configuration using modeling software and by a semi-empirical molecular orbital (MO) calculation method. Fig. 6 shows the optimized geometries, and Table 3 summarizes the dihedral angles between the least square planes of the naphthalene ring and the phenyl ring of the 2-, 4- or 7-position, where the dihedral angles were calculated by using the atomic coordinates obtained through the geometry optimization. Table 3 includes also the dihedral angles of those in 3b and 4b of the optimized structures with a keto-hydrazone configuration through the same calculation manner for comparison. These results indicate that both of the two phenyl rings attached to the naphthalene ring via the carboxamide groups are twisted relative to the naphthalene plane, while the phenyl ring attached to the naphthalene ring via the hydrazone group is less twisted to the naphthalene ring. The twist at the 2-position is more or less small compared with that at the 7-position in 3a and 4a.

The above geometry supports the possibility that the πconjugation or the chromophore system of **3a** and **4a** is analogous to that of **3b** and **4b**, and is constituted substantially with the naphthol ring, 2-phenylcarboxamide and 4-phenylhydrazone. Involvement of 7-phenylcarboxamide in the chromophore systems of **3a** and **4a** should be therefore much less compared with that of 2-phenylcarboxamide. If **3a** and **4a** form molecular crystals with no

strong intermolecular interaction like other azonaphtharylamide pigments [6-12], their color properties originate in their isolated molecular structures and should be similar to those in solutions. The above chromophoric analogy should be responsible for the resemblance in the contours of the optical absorption spectra between **3a** and **3b** and between **4a** and **4b**.

The longest wavelength bands of **3a** and **4a** calculated by the semi-empirical MO method are summarized in Table 4. They appeared in higher energy regions than those of the experimentally observed bands. Such shifts toward higher energy regions are generally observed in semi-empirical calculations [13,14] and the shift can be 110 nm [14]. An approximately linear correlation between the calculated wavelengths and the wavelengths of the peaks/shoulders in the optical absorption spectra of **3a** and **4a** also supports the validity of the analysis based on the semi-empirical MO method.

The computations indicate that the longest wavelength bands for **3a** and **4a** are due to  $\pi\pi^*$  transitions from the HOMO or orbitals close to it to the LUMO or orbitals close to it. The molecular orbitals involved in the transitions are shown in Figs. 7 and 8 for **3a** and **4a**, respectively. These figures illustrate that the following orbitals contain electron localization on the 7-phenylcarboxamide group: (**3a**) HOMO-2, LUMO+1 and LUMO+2, and (**4a**) HOMO-2, HOMO-1, LUMO+2 and LUMO+3. Therefore, although the 7-substituent hardly contributes to expansion of the chromophore system, the electron localization on the 7-substituent surely contributes to increment of transition probability, inducing the

hyperchromic effect as observed with 3a and 4a.

#### 2.5 Light fastness of 3a and 4a

The durability of organic pigments, both azo and heterocyclic pigments, has been discussed in relation to intramolecular and/or intermolecular interactions, including hydrogen bonding,  $\pi\pi$ stacking, and van der Waals contact. A strong intermolecular hydrogen bond binds diketopyrrolopyrrole or quinacridone molecules in their crystal structures, which is one of the important factors for imparting durability to these pigments [15,16]. Concerning conventional 7-unsubstituted azonaphtharylamide pigments, no strong intermolecular hydrogen bond network has been found. Alternatively, stabilization of the bifurcated intramolecular hydrogen bonds formed among the keto-hydrazone and 2-carboxamide groups has been proposed to explain the durability [6,7]. It has also been pointed out that increase in the number of amide groups tends to improve the technical performance of the azonaphtharylamide pigments, e.g., resistance to light, heat, solvent and/or migration [2,6,7], as experimentally demonstrated for the aforementioned Group 2 pigments.

Since **3a** and **4a** possess the two amide groups, these pigments are expected to outperform in durability **3b** and **4b**, which belong to conventional Group 1 pigments. We therefore evaluated light fastness of **3a**, **3b**, **4a**, and **4b** using transparent films of an acrylic resin in which the pigments had been dispersed. Changes in the absorption spectra of the films in the

visible light region were monitored while they were photo-irradiated at the intensity of 75 mW/cm<sup>2</sup> (400 to 1100 nm) for 48 hours using a Xe lamp as the light source. Fig. 9 shows the changes in the absorbance of the films at their absorption maxima. The results show that **3a** and **4a** have higher light fastness than **3b** and **4b**, which is attributable to the increased number of the amide groups, as observed with different pigments [2,6,7]. The excellent light fastness of **3a** and **4a** are suggested also in a reference [3]. Improved chemical stability of the pigments will also enhance their heat resistivity. This tendency was confirmed by the increase in the decomposition points of **3a** and **4a** compared with those of **3b** and **4b**, as shown in Table 5. The improved durability of **3a** and **4a** against light and heat is the most important advantages of these pigments for practical applications [3].

#### 3. Conclusion

We studied effect of a 7-substituent of two7-substituted azonaphtharylamide pigments. The pigments were obtained using the coupling component,

3-hydroxy-N2,N7-diphenyl-naphthalene-2,7-dicarboxamide, derived from

3-hydroxy-2,7-naphthalene dicarboxylic acid. Presence of 7-phenycarboxamide distinguishes

the pigments from conventional azonaphtharylamide pigments derived from

3-hydroxy-2-naphthoic acid. The 7-substituted pigments exhibited higher insolubility, higher

decomposition points, and relatively lower crystallinity than those of the 7-unsubstituted counterparts. The optical absorption spectra of the 7-substituted pigments in solution showed a hyperchromic effect and did not show a bathochromic shift compared with the 7-unsubstituted counterparts. Molecular geometry optimizations through semi-empirical MO calculations showed that extent of the chromophore system of the 7-substituted pigments is comparable with those of the counterparts, accounting for absence of the bathochromic shift. The calculations elucidated the hyperchromic effect, which is provided by involvement of the 7-substituted ones. The 7-substituted pigments demonstrated durability superior to that of the 7-unsubstituted ones. Consequently, the 7-substituted pigments are expected to create a new subclass of azonaphtharylamide pigments.

#### 4. Experimental

#### 4.1 Materials

All the chemicals were purchased from Tokyo Kasei Co., Ltd. except

3-hydroxy-2,7-naphthalene dicarboxylic acid. The dicarboxylic acid was purchased from

Wako Pure Chemical Industries. Solvent-soluble acrylic resin BR-87 was obtained from

Mitsubishi Rayon Co., Ltd.

#### 4.2 Instruments

Decomposition points were measured with Bruker TG-DTA2000SA. Mass spectra were taken on JEOL JMS-700 (EI-TOF MS) and Bruker Ultraflex TOF/TOF MS (MALDI-TOF MS). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL JNM-ECS400 Spectrometer. UV-Vis absorption spectra were measured with HITACHI U-3310 Spectrophotometer. Powder X-ray diffraction patterns were evaluated with Rigaku MiniFlex600 (Cu K<sub>a</sub> 30kV/15mA). Light fastness of the pigments was evaluated with ASAHI Spectra Solar Simulator HAL-320.

#### 4.3 Synthesis of 2

Slurry was made using 3-hydroxy-2,7-naphthalene dicarboxylic acid (20.0 g, 0.09 mol) with 80 g of toluene. Aniline (48.1 g, 0.52 mol) was dissolved in 125.0 g of toluene at room temperature. Phosphorus trichloride (11.8 g, 0.09 mol) was added dropwise to the aniline solution and the mixture was filtrated. The filtrate obtained was then poured into the slurry and the reaction mixture was kept at 110°C for 3 hours while stirring, and then filtrated. The white powder, 3-hydroxy-N2,N7-diphenyl-naphthalene-2,7-dicarboxamide, was washed with methanol. Yield was 29.0 g (84.2 mol% relative to 3-hydroxy-2,7-dicarboxylic acid); <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$ 7.12 (t, 2H, *J* = 7.4 Hz), 7.16 (t, 2H, *J* = 7.4 Hz), 7.38 (t, 2H, *J* = 7.4 Hz), 7.40 (t, 2H, *J* = 7.4 Hz), 7.42 (s, 1H), 7.79 (d, 2H, *J* = 7.4 Hz), 7.83 (d, 2H, *J* =

7.4Hz), 7.90 (d, 1H, *J* = 7.6 Hz), 8.04 (dd, 1H, *J* = 7.6 Hz, 1.8 Hz), 8.61 (d, 1H, *J* = 1.8 Hz), 8.61 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-d6) δ110.36, 120.22, 120.25, 123.38, 123.52, 123.97, 125.72, 125.86, 126.34, 128.54, 128.73, 128.96, 129.90, 131.58, 136.93, 138.39, 139.16, 155.05, 165.02, 165.24.

#### 4.4 Preparation of 2,5-dichloroaniline diazonium fluoroboric salt for 3a and 3b

2,5-Dichloroaniline (12.5 g, 0.08 mol) was put into a flask (300 ml) with 62.5 g of water and acetic acid (4.6 g, 0.08 mol). 35% Hydrochloride (16.1 g, 0.15 mol) was added dropwise to the above mixture keeping at 50°C. 35% Hydrochloride (16.1 g, 0.15 mol) and 50.0 g of water was then further added at 45°C. After cooling the system below 0°C, 16% of aqueous solution of sodium nitrite (0.08 mol) was added dropwise to the system while stirring. After removal of insoluble substances and wash with 12.5 g of water, the intermediate was kept below 5°C, and 42% fluoroboric acid (30.4 g, 0.16 mol) was added dropwise, and then filtrated. The precipitate was washed with water and subsequently with isopropyl alcohol, and dried. White crystalline powder was obtained. The yield was 17.8 g (98.7%). The salt was used for following diazotization without identification.

#### 4.5 Preparation of 2-metyl-5-nitoroaniline diazonium fluoroboric salt for 4a and 4b

2-Methyl-5-nitroaniline (12.5 g, 0.08 mol) was put into a flask (300 ml) with 125.0 g of

water and 25.7 g of 35% hydrochloride. 16% Sodium nitrite (39.0 g, 0.09 mol) was added dropwise to the above mixture keeping the system below 5°C. After removing insoluble substances, the intermediate was kept below 5°C, and 42% fluoroboric acid (32.4 g, 0.17 mol) was added dropwise, and then filtrated. The precipitate was washed with water, and subsequently isopropyl alcohol, and dried. White crystalline powder was obtained. The yield was 19.8 g (98.4%). The salt was used for following diazotization without identification.

#### 4.6 Synthesis of 3a

3-Hydroxy-N2,N7-diphenyl-naphthalene-2,7-dicarboxamide (3.0 g, 0.008 mol) was charged into a flask (100 ml) with N-methylpyrrolidone (NMP, 24.0 g) and sodium hydroxide (0.69 g, 0.017 mol). The mixture was stirred at 40°C and then cooled below 5°C. After 2,5-dichloroaniline diazonium fluoroboric salt (2.46 g, 0.009 mol) had been added to the flask while stirring and keeping the temperature below 5°C, the solution was stirred overnight at room temperature, and neutralization using acetic acid was performed. The red powder generated was filtrated and washed sequentially with acetone, methanol and water. Finally, the powder was dispersed in methanol, filtrated, and dried in an oven at 80°C. The powder thus obtained (2.6 g, 0.005 mol) was further treated in N,N-dimethylformamide (DMF, 20 g) at 120-130°C for 3 hours while stirring. The product was washed with DMF and methanol and dried in an oven at 80°C. Yellowish red

4-(2,5-dichlorophenyl)azo-3-hydroxy-N2,N7-diphenylnaphthalene-2,7-dicarboxamide (2.2 g) was obtained as an extremely insoluble crystalline powder. Yield 50.5%; decomposition point 339°C; MALDI-TOF MS m/z 553.040 [M-H]<sup>-</sup> (100%), calcd for [C<sub>30</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>3</sub>]<sup>-</sup> 553.083.

#### 4.7 Synthesis of 4a

3-Hydroxy-N2,N7-diphenyl-naphthalene-2,7-dicarboxamide (3.0 g, 0.008 mol) was charged into a flask (100 ml) with NMP (24.0 g) and sodium hydroxide (0.69 g, 0.017 mol). The mixture was stirred at 40°C and then cooled below 5°C. After 2-methyl-5-nitroaniline diazonium fluoroboric salt (2.36 g, 0.009 mol) had been added to the flask while stirring and keeping the temperature below 5°C, the solution was stirred overnight at room temperature, and neutralization using acetic acid was performed. The red powder generated was filtrated and washed sequentially with acetone, methanol and water. Finally, the powder was dispersed in methanol, filtrated, and dried in an oven at 80°C. The powder thus obtained (2.6 g, 0.005 mol) was further treated in DMF (20 g) at 120-130°C for 3 hours while stirring. The product was washed with DMF and methanol and dried in an oven at 80°C. Bluish red

4-(2-methly-5-nitrophenyl)azo-3-hydroxy-N2,N7-diphenylnaphthalene-2,7-dicarboxamide (2.4g) was obtained as an extremely insoluble crystalline powder. Yield 56.1%; decomposition point 320°C; MALDI-TOF MS m/z 544.120 [M-H]<sup>-</sup> (100%), calcd for [C<sub>31</sub>H<sub>22</sub>N<sub>5</sub>O<sub>5</sub>]<sup>-</sup> 544.162.

The following syntheses of **3b** and **4b** were carried out to obtain chemically pure samples. Commercially available ones may contain additives such as dispersants.

#### 4.8 Synthesis of **3b**

2-Hydroxy-3-naphthoic acid anilide (2.5 g, 0.010 mol) was charged into a flask (100 ml) with NMP (24.0 g) and sodium hydroxide (0.69 g, 0.017 mol). The mixture was stirred at 40°C and then cooled below 5°C. After 2,5-dichloroaniline diazonium fluoroboric salt (2.97 g, 0.011 mol) had been added to the flask while stirring and keeping the temperature below 5°C, the solution was stirred overnight at room temperature, and neutralization using acetic acid was performed. The red powder generated was filtrated and washed sequentially with acetone, methanol and water. Finally, the powder was dispersed in methanol, filtrated, and dried in an oven at 80°C. The powder thus obtained (2.6 g, 0.005 mol) was further treated in DMF (20 g) at 120-130°C for 3 hours while stirring. The product was washed with DMF and methanol and dried in an oven at 80°C. Yellowish red

4-(2,5-dichlorophenyl)azo-3-hydroxy-N-phenylnaphthalene-2-carboxamide (2.5 g) was obtained. Yield 60.3%; decomposition point 305°C; EI-TOF MS m/z 435.0538, calcd for C<sub>23</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub> 435.0541.

4.9 Synthesis of 4b

2-Hydroxy-3-naphthoic acid anilide (2.5 g, 0.001 mol) was charged into a flask (100 ml) with NMP (20.0 g) and sodium hydroxide (0.84 g, 0.021 mol). The mixture was stirred at 40°C and then cooled below 5°C. After 2-methyl-5-nitroaniline diazonium fluoroboric salt (2.86g, 0.011mol) had been added to the flask while stirring and keeping the temperature below 5°C, the solution was stirred overnight at room temperature, and neutralization using acetic acid was performed. The red powder generated was filtrated and washed sequentially with acetone, methanol and water. Finally, the powder was dispersed in methanol, filtrated, and dried in an oven at 80°C. The powder thus obtained (2.6 g, 0.005 mol) was further treated in DMF (20 g) at 120-130°C for 3 hours while stirring. The product was washed with DMF and methanol and dried in an oven at 80°C. Bluish red

4-(2-methyl-5-nitrophenyl)azo-3-hydroxy-N-phenylnaphthalene-2-carboxamide (2.5g) was obtained. Yield 61.7%; decomposition point 310°C; EI-TOF MS m/z 426.1335, calcd for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub> 426.1328.

#### 4.10 MO and CI calculations

Semi-empirical MO calculation with the Hamiltonian, AM1, was employed in the present study, followed by singly excited configuration interaction calculations with the INDO/S method using 20 occupied and vacant orbitals. All calculations were done with SCIGRESS MO Compact (Fujitsu Ltd.). Each compound was modeled initially with the modeling

software DS Modeling (Accelrys Inc.) and then by geometry optimization during the MO calculation with AM1.

#### 4.11 Evaluation of light-fastness of **3a** to **4b**

The following materials were put in a 70 ml mayonnaise bottle: pigment (0.12 g), zirconia beads ( $\phi$ 0.3 mm, 3 g), solvent-soluble acrylic resin BR-87 (5.0 g), and ethyl acetate (2.4 g). The materials were mixed with a ball mill by rotating the bottle for 5 hours to disperse the pigment. The ink obtained was dropped on a slide glass and spin-coated (500 rpm) to form a transparent thin film. The films were placed in Solar Simulator HAL-320 (Xe-lamp, irradiation intensity 75mW/cm<sup>2</sup> (400 to 1100 nm) to be irradiated for 48 hours in air.

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Fig.1 Chemical structures of starting compound 1, coupling component 2 derived from 1, azo pigments 3a and 4a, which were synthesized from 2; and 3b (C. I. Pigment Red 2) and 4b (C. I. Pigment Red 22) used as reference. For easy comparison with 2, the structures of 3a, 3b, 4a and 4b are depicted in the hydroxy-azo configurations, although they are believed to have the keto-hydrazone configurations.



**Fig. 2** X-ray diffraction patterns of **3a** and **3b** which were heat-processed at 120-130°C in N,N-dimethylformamide for 3 hours for crystal growth promotion.



**Fig. 3** X-ray diffraction patterns of **4a** and **4b** which were heat-processed at 120-130°C in N,N-dimethylformamide for 3 hours for crystal growth promotion.



Fig. 4 Optical absorption spectra of 3a and 3b in N-methylpyrrolidone.





Fig. 6 Optimized molecular geometries of 3a and 4a having keto-hydrazone configurations.

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Fig. 7 MOs of 3a (keto-hydrazone form) involved in the transitions for longest wavelengths (see Table 4 also).



Fig. 8 MOs of 4a (keto-hydrazone form) involved in the transitions for longest wavelengths (see Table 4 also).



**Fig. 9** Light fastness of **3a**, **3b**, **4a** and **4b**. The pigments were dispersed in acrylic films and irradiated with a Xe-lamp (75 mW/cm<sup>-2</sup>; 400 to 1100 nm). For each sample, the absorbance at the peak absorption wavelength is plotted for irradiation periods of 24 and 48 h. The absorbance is normalized by the absorbance of the sample before photoirradiation.



Scheme 1 Syntheses of coupling component 2 and azo pigments 3a and 4a starting from 3-hydroxy-2,7-naphthalene dicarboxylic acid 1. Aniline 6, its fluoroboric salt 7 and the pigment structure are given in a general formula.  $R_c^{1}$ ,  $R_c^{2}$  and  $R_c^{3}$  on 6, and  $R_D^{1}$ ,  $R_D^{2}$  and  $R_D^{3}$  on 7 represent substituents available including hydrogen (3a:  $R_D^{1} = R_D^{3} = Cl$ , and  $R_c^{1} = R_c^{2} = R_c^{3} = R_D^{2} = H$ ; and 4a:  $R_D^{1} = CH_3$ ,  $R_D^{3} = NO_2$ , and  $R_c^{1} = R_c^{2} = R_c^{3} = R_D^{2} = H$ ).

$\lambda_{max}^{abs}$	/nm	$\epsilon_{max}/dm^3$ i	nol <sup>-1</sup> cm <sup>-1</sup>
3a	3b	3a	3b
569	574	18500	16900
543	545	19200	17600
<sup>a</sup> 498sh	<sup>a</sup> 508sh	15000	14900
<sup>a</sup> 387sh	<sup>a</sup> 380sh	15500	16700
370	368	17100	11900

Table 1 Wavelengths of optical absorption maxima and molar extinction coefficients of 3a and 3b in

N-methylpyrrolidone.

	545	19200	17600
<sup>a</sup> 498sh	<sup>a</sup> 508sh	15000	14900
<sup>a</sup> 387sh	<sup>a</sup> 380sh	15500	16700
370	368	17100	11900
<sup>a</sup> sh: shoulder a	bsorption		
Table 2 Way	velengths of c	optical absorp	otion maxima
Table 2 Way	velengths of c	optical absorp	otion maxima
Table 2 Way N-methylpy λ <sub>nax</sub> <sup>abs</sup>	velengths of c rrolidone.	pptical absorr <sub>قnax</sub> /dm <sup>3</sup> r	nol <sup>-1</sup> cm <sup>-1</sup>
Table 2 Way       N-methylpy $\lambda_{max}^{abb}$ 4a	/elengths of c rrolidone. /nm <b>4b</b>	pptical absorp ε <sub>nax</sub> /dm <sup>3</sup> r 4a	otion maxima nol <sup>-1</sup> cm <sup>-1</sup> <b>4b</b>
Table 2 Wav N-methylpy λ <sub>nax</sub> <sup>abs</sup> 4a <sup>a</sup> 569sh	/elengths of c rrolidone. /nm 4b °578sh	pptical absorp <u>ε<sub>max</sub>/dm<sup>3</sup> r</u> <u>4a</u> 14100	otion maxima nol <sup>-1</sup> cm <sup>-1</sup> <u>4b</u> 8600
Table 2 Way N-methylpy λ <sub>nax</sub> <sup>abs</sup> 4a <sup>a</sup> 569sh 533	/elengths of c rrolidone. /nm 4b <sup>a</sup> 578sh 524	pptical absorp <u>ε<sub>nax</sub>/dm<sup>3</sup> r</u> <u>4a</u> 14100 15700	nol <sup>-1</sup> cm <sup>-1</sup> 4b 8600 11700
Table 2 Wav           N-methylpy           λmax <sup>abs</sup> 4a <sup>a</sup> 569sh           533 <sup>a</sup> 501sh	/elengths of c rrolidone. /nm 4b *578sh 524 *498sh	<u>ε<sub>nax</sub>/dm<sup>3</sup> r</u> <u>4a</u> 14100 15700 15200	nol <sup>-1</sup> cm <sup>-1</sup> 4b 8600 11700 10900
Table 2 Wav           N-methylpy           λmax <sup>abs</sup> 4a <sup>a</sup> 569sh           533 <sup>a</sup> 501sh <sup>a</sup> 407sh	velengths of c rrolidone. //nm 4b *578sh 524 *498sh *382sh	pptical absorp <u>smax/dm<sup>3</sup> r</u> <u>4a</u> 14100 15700 15200 10400	nol <sup>-1</sup> cm <sup>-1</sup> 4b 8600 11700 10900 6700

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$\lambda_{max}^{ab}$	s/nm	$\epsilon_{max}/dm^3 m$	nol <sup>-1</sup> cm <sup>-1</sup>
4a	4b	4a	4b
<sup>a</sup> 569sh	<sup>a</sup> 578sh	14100	8600
533	524	15700	11700
<sup>a</sup> 501sh	<sup>a</sup> 498sh	15200	10900
<sup>a</sup> 407sh	<sup>a</sup> 382sh	10400	6700
389sh	364	14000	8300

Table 3 Dihedral angles between the least square planes of the naphthalene ring and the phenyl rings of 3a, 3b, 4a and 4b. The least square planes were calculated by using the atomic coordinates obtained in the geometry optimization.

Position of a phenyl substituent		Dihedral angle vs. n	aphthalene (degree )	
(on a naphthalene ring)	<b>3</b> a	3b	<b>4</b> a	4b
-4	17.5	15.9	21.1	14.0
2	29.4	27.6	28.0	27.2
7	30.3	-	31.2	_

Compound	Absorption [nm]	Oscillator strength	CI component <sup>a</sup>			Absorption band in N-methylpyrrolidon [nm]	
	417.0	06084	HOMO	$\rightarrow$	LUMO	(58%)	
	353.7	02057	HOMO-3	$\rightarrow$	LUMO	(36%)	470 590
	210.8	0.350	HOMO	$\rightarrow$	LUMO+1	(22%)	470-380
20	510.8	0204	HOMO-3	$\rightarrow$	LUMO+1	(15%)	
Ja	280.5	0410	HOMO-2	$\rightarrow$	LUMO	(27%)	
			HOMO	$\rightarrow$	LUMO+1	(15%)	250,400
	268.6	04759	HOMO	$\rightarrow$	LUMO+2	(15%)	550-400
			HOMO-2	$\rightarrow$	LUMO	(11%)	
	414.0	05962	HOMO-1	$\rightarrow$	LUMO	(50%)	
	355.4	02283	HOMO-3	$\rightarrow$	LUMO	(47%)	470.590
	200.7	0770	HOMO-6	$\rightarrow$	LUMO	(17%)	470-380
4a	309.7	0.262	HOMO-1	$\rightarrow$	LUMO+2	(17%)	
	285.6	01256	HOMO-2	$\rightarrow$	LUMO	(52%)	_
270.7 269.3	270.7	03100	HOMO-1	$\rightarrow$	LUMO+2	(25%)	350-400
	269.3	04977	НОМО	$\rightarrow$	LUMO+3	(25%)	-

Table 4 Optical absorption spectra of 3a and 4a in the ketohydrazone-form calculated by the semi-empirical MO method and their band positions experimentally observed in N-methylpyrrolidone.

Table 5 Decomposition points of 3a, 3b,	4a and 4b evaluated by TG-DTA.

Compound	<b>3</b> a	3b	4a	4b
Decomposition point (°C)	339	305	320	310
<b>U</b>				

Graphical abstract



#### Highlight

- ► Azonaphtharylamide pigments having 2- and 7-substituents were studied.
- The pigments exhibited a hyperchromic effect and no bathochromic shift compared with the 7-unsubstituted counterparts.

- Light and heat fastness of the pigments outperformed those of the counterparts.
- The pigments are expected to form a new subclass of the azo pigments.