Design, synthesis, characterization of water-soluble indophenine dyes and their application for dyeing of wool, silk and nylon fabrics

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CRediT authorship contribution statement

Jinfang Cai: Methodology; Validation; Investigation; Visualization; Data Curation; Writing-Original Draft;

Hua Jiang: Conceptualization; Methodology; Software; Writing-Review & Editing

Weiguo Chen: Supervision; Writing-Review & Editing

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1 Design, synthesis, characterization of water-soluble indophenine dyes and their application for

- 2 dyeing of wool, silk and nylon fabrics
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Abstract: In view of our continuing interests in application of quinoidal heterocyclic structure into 10 textile dyestuffs, we report here the design and synthesis of four new water-soluble dyes D1-D4 that 11 based on indophenine structure and bearing alkyl chains with different lengths. Their properties on 12 geometry, electronic structure, solubility, thermal stability and absorption spectra have been well 13 investigated. Then, the dveing ability of **D1-D4** is checked by application into dveing of wool, silk 14 and nylon fabrics and is compared with three commercial acid dyes. The effect of quinoidal 15 coplanarity of indophenine backbone and alkyl substituents on dyeing performance has been 16 revealed. Our study clearly demonstrates that the introduction of rigid quinoidal heterocyclic 17 structure with high coplanarity as the chromophore backbone is an efficient method for the design of 18 high-performance acid dyestuffs in terms of exhaustion, coloring strength and wet fastness. 19

20 *Keywords*: Indophenine; Sulfonation; Absorption; Acid dyes; Dyeing properties

22 **1. Introduction**

Conventionally, acid dyes are widely applied on dyeing of wool, silk, nylon fabrics under acidic 23 conditions, and coloration of leather, paper, cosmetics, ink, etc. as well [1, 2]. The acid dyes can be 24 structurally classified as azo dyes [3-8], anthraquinone dyes [9, 10], triphenylmethane dyes [11, 12], 25 nitro dyes [13], etc. Among them, acid dyes that containing heterocyclic moiety are acknowledged 26 with high molar extinction coefficient, high color strength, and good dyeing performance. The 27 common design strategy for heterocyclic acid dyes is to construct azo chromophore by using 28 heterocyclic units as diazo or coupling components [14-16]. Direct adoption of heterocyclic 29 structures with large π -conjugation system as chromophore meets the difficulty of complex multistep 30 31 synthesis [17, 18].

Fabrics can be dyed with acid dyes through ionic bond as well as Van der Waals' force and hydrogen bond. Unfortunately, these bonds are easily broken in hot wet conditions leading to relatively poor wet fastness [19, 20]. The invention of acid mordant dyes and *pre*-metalized acid dyes indeed largely improves the wet fastness [21-23]. However, the potential heavy-metal pollution existed in dyed fabrics and waste water has made this dyeing technology limited socially, politically and legally [24, 25]. Thus, the development of environmentally friendly and high-performance acid dyestuffs becomes the common goal in this research field.

Judicious molecular design methods for acid dyes to improve the wet fastness include following aspects. The first way is to decrease the dyes' solubility and increase the affinity of dyes-to-fiber through hydrophobic interaction by introduction of alkyl chain [26, 27]. The sulfonic acid groups on the dye backbone provide the possibility to form electrostatic interaction with amino groups in fibers

but the hydrophilicity of sulfonic acid groups might migrate the dye molecules out of the fiber under 43 wet treatment. Thus, it is expected that reducing the weight ratio of sulfonic acid groups in molecule 44 ought to improve the wet fastness. Introduction of coplanar structure into dye molecule is another 45 efficient method. The stronger intermolecular interactions between dve and fiber generated by the 46 high molecular coplanarity are thought to be helpful for obtaining better wet fastness. Usually, the 47 construction of chromophore's structure with high coplanarity can be achieved either by directly 48 using the planar synthetic building block [17] or by ring closure with intramolecular weak 49 interactions [5]. 50

In the effort of searching for new chromophores for high-performance textile dyes, quinoidal 51 heterocyclic compounds have attracted our attention because of their unique characteristics [28, 29]. 52 The quinoidal heterocyclic structure possesses a highly rigid backbone that all atoms on the 53 quinoidal π -conjugation system are in the same plane [30]. Besides, most of the quinoidal hetercyclic 54 compounds are highly colored and the highest molar extinction coefficient can be up to 2×10^5 55 L·mol⁻¹cm⁻¹ [31, 32]. In this context, we envisage that the introduction of quinoidal heterocyclic 56 backbone should be an effective way for the design of high-performance textile dyestuffs. In 2018, 57 we reported the application of dicyanomethylene or (alkoxy)acylcyanomethylene endcapped 58 quinoidal bithiophenes (**QBT** series) into dyeing poly(ethylene terephthalate) (PET) fabrics [33]. As 59 a result, the pink/red dyed fabrics exhibited high exhaustion up to 97% and good to excellent fastness 60 to washing, rubbing and sublimation. Very recently, we also presented the use of indophenine 61 derivatives for dyeing of PET fabrics and achieved even better anti-thermomigration fastness than 62 conventional azo or anthraquinone dyes [34]. As confirmed by our experimental and theoretical 63 studies, there existed large dye-fiber interactions between these quinoidal heterocyclic molecules and 64

PET fibers, which could be regarded as the reason for high fastness level. However, the attempt of
designing hydrophilic dyestuffs with quinoidal heterocyclic moiety and the study of their dyeing
application have not been reported.

As the extension of our work, we report in the present study the design and synthesis of four new 68 water-soluble indophenine dyes D1-D4 (Fig. 1) and the feasibility of dyeing on several fibers. The 69 following principles are considered in the design of indophenine dyes molecules. (i) The two fused 70 benzene rings in indophenine backbone are electron-rich moieties, which are suitable for the 71 introduction of sulfonic acid groups by sulfonation reaction. (ii) Alkyl chains can be easily 72 introduced at the nitrogen atoms, hence making it possible to easily fine-tune the intermolecular 73 interaction between dye molecule and fiber. (iii) The facile synthesis of indophenine dyes by 74 so-called "indophenine reaction" provides the convenience for scale-up production [35], therefore 75 facilitating the application research. Our laboratory scale tests demonstrated that these dyes had the 76 ability of dyeing wool, silk and nylon with deep blue shade. As predicted, the fabrics dyed with 77 indophenine dyes have even better wet fastness properties than that dyed with selected commercial 78 acid dyes. Subsequently, structure-property relationships of indophenine quinoidal backbone and 79 alkyl substituents on dyes' absorption, exhaustion, dyeing rate, build-up and fastness properties have 80 been systematically studied. 81

82 **2. Experimental section**

83 2.1. Materials and instrumentation

The chemicals for synthesis, including isatin, ethyl bromide, hexyl bromide, decyl bromide, thiophene, *etc.* were purchased from Adamas Reagent Co., Ltd., and used without further purification.

1-Ethylindoline-2,3-dione [34], 1-hexylindoline-2,3-dione [36], and 1-decylindoline-2,3-dione [37] were synthesized according to reported papers. Anhydrous toluene for synthesis were pre-treated by distillation and stored under nitrogen. Twilled wool fabrics (200 g/m²), plain silk fabrics (40 g/m²) and knitted nylon 66 fabrics (230 g/m²) were obtained commercially. The three blue commercial acid dyes, **D5-D7**, which represented azo, anthraquinone and triphenylmethane dyes respectively, were purified by DMF-ether method [38] and used as reference dyes. The chemical structures of **D1-D4** as well as the reference dyes **D5-D7** were shown in **Fig. 1**.

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Fig. 1 Molecular structures of designed dyes D1-D4 and reference dyes D5-D7

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temperature in DMSO- d_6 . Infrared (IR) spectra (4000-400 cm⁻¹) were recorded using a Nicolet 98 FT-IR 170X spectrophotometer on KBr disks. Electrospray ionization mass spectra (ESI-MS) were 99 recorded on a Thermo Lcq Fleet mass spectrometer in a scan range of 200-2000 amu. Accurate mass 100 data were obtained by high resolution mass spectrometry performed on a SYNAPT-G2-S HDMS 101 spectrometer. The thermal stability of all the dye samples was investigated using TGA under N₂. The 102 degradation temperature (T_d) was obtained by determining the slope of the portion where the weight 103 percentage decreased sharply on the TGA graph. UV-vis spectra were measured by using Shimadzu 104 UV-2600 dual-beam spectrophotometer. Dyeing of wool/silk/nylon fabrics was operated on 105 Chain-Lih DYE-24 adjustable dyeing machine. The K/S value as well as the color parameters of the 106 dyed fabrics was measured by Datacolor SF 600X spectrophotometer. 107

108 2.2 Synthesis of compounds 5-8

Concentrated sulfuric acid (15 mL, 98wt%) was added dropwisely to a solution of isatins (20 109 mmol) and thiophene (40 mmol, 3.37 g) in toluene (40 mL) at 0 °C. The color of the mixture became 110 dark blue. The mixture continued to react at 0 °C for 3 h until the isatin derivative was totally 111 consumed. For the synthesis of compound 5, the transparent toluene was removed and the residue 112 was poured into icy water (200 mL). After filtration, the crude solid was washed with an excess of 113 ethanol, hexane dichloromethane successively, 114 water, and and dried in vacuum. 3,3'-([2,2'-Bithiophenylidene]-5,5'-divlidene)bis(indolin-2-one) (5), dark blue solid [34], 3.33 g, 78%. 115 Mp: >300 °C. ESI-MS (100%, negative) m/z = 425 ([M–H]⁻); ESI-HRMS (100%, positive) Calcd. 116 for $C_{24}H_{14}N_2O_2S_2$: 426.0497 ([M]⁺), found: 426.0497; IR (KBr) v = 1670 cm⁻¹ (C=O). 117

118 For compounds 6-8, the reaction mixture was added into icy water (150 mL) and extracted with

$CH_2Cl_2(100)$) mL×3). 7	Гhe organic	layer was	combine	d, and	washed	with s	satura	ted	brine.	The	crude
product was	s obtained	by evapora	tion of th	e solvent	under	reduced	press	sure, a	and	could	be f	further

- purified by column chromatography (eluent: petroleum/EtOAc = 10/1 then CH₂Cl₂).
- 122 3,3'-([2,2'-Bithiophenylidene]-5,5'-diylidene)bis(1-ethylindolin-2-one) (6), dark blue solid [34],
- 123 3.19 g, 66%. Mp: 252–254 °C. ESI-MS (100%, negative) m/z =482 ([M]⁻); ESI-HRMS (100%, 124 positive) Calcd. for C₂₈H₂₂N₂O₂S₂: 482.1123 ([M]⁺), found: 482.1132; IR (KBr) v =1669 cm ⁻¹
- 125 (C=O).

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126 3,3'-([2,2'-Bithiophenylidene]-5,5'-diylidene)bis(1-hexylindolin-2-one) (7), dark blue solid, 5.06 g,

85%. Mp: 202–204 °C. ESI-MS (100%, positive) m/z = 594 ([M]⁺); ESI-HRMS (100%, positive)

- 128 Calcd. for $C_{36}H_{38}N_2O_2S_2$: 594.2369 ([M]⁺); found: 594.2370. IR (KBr) $v = 1670 \text{ cm}^{-1}$ (C=O).
- 129 3,3'-([2,2'-Bithiophenylidene]-5,5'-diylidene)bis(1-decylindolin-2-one) (8), dark blue solid, 6.29 g, 130 89%. Mp: 180–182 °C. ESI-MS (100%, positive) m/z = 706 ([M]⁺); ESI-HRMS (100%, positive) 131 Calcd. for C₄₄H₅₄N₂O₂S₂: 706.3639 ([M]⁺); found: 706.3631. IR (KBr) v = 1669 cm⁻¹ (C=O).
- 132 2.3 Synthesis of dyes **D1-D4**

The indophenine intermediates **5-8** (2.56 mmol) was carefully added in batch to conc. H_2SO_4 (15.6 mL, 0.256 mol, 98wt%) under room temperature. The reaction was stirred at 60 °C for 4 h. After the reaction was completed, the solution was poured onto ice, and sodium chloride was added to promote the precipitation of target compounds. Finally, the precipitation was filtered, washed with saturated brine and dried.

138 **D1**, dark blue solid, 1.44 g, 96%. Mp: >300 °C. ESI-MS (100%, negative) m/z = 292

139 $(1/2[M-2H]^{2-})$, 585 $([M-H]^{-})$; ESI-HRMS (100%, negative) Calcd. for C₂₄H₁₃N₂O₈S₄ 584.9549 140 $([M-H]^{-})$, found: 584.9630; IR (KBr) v = 1622 cm⁻¹ (C=O).

141 **D2**, dark blue solid, 1.60 g, 97%. Mp: >300 °C. ESI-MS (100%, negative) m/z = 320142 $(1/2[M-2H]^{2-})$, 641 ([M-H]⁻); ESI-HRMS (100%, negative) Calcd. for C₂₈H₂₁N₂O₈S₄: 641.0176 143 ([M-H]⁻), found: 641.0232; IR (KBr) v = 1637 cm⁻¹ (C=O).

144 **D3**, dark blue solid, 1.87 g, 97%. Mp: >300 °C. ESI-MS (100%, negative) m/z = 376145 $(1/2[M-2H]^{2-})$; ESI-HRMS (100%, negative) Calcd. for C₃₆H₃₇N₂O₈S₄: 753.1427 ([M-H]⁻), found: 146 753.1487; IR (KBr) v = 1637 cm⁻¹ (C=O).

147 **D4**, dark blue solid, 2.04 g, 92%. Mp: >300 °C. ESI-MS (100%, negative) m/z = 432148 $(1/2[M-2H]^{2-})$, 887 ([M-H]⁻, in the form of mono sodium salt); ESI-HRMS (100%, negative) Calcd. 149 for C₄₄H₅₃N₂O₈S₄: 865.2685 ([M-H]⁻), found: 865.2855; IR (KBr) v = 1639 cm⁻¹ (C=O).

150 2.4 Synthesis of compounds 9-12

151 Conc. H_2SO_4 (1 mL) was added to isatin derivative (2 mmol) under room temperature. The 152 reaction was stirred at 60 °C for 3 h. After the reaction was completed, the solution was poured onto 153 crushed ice, followed by filtration and washing with icy saturated brine. The crude product could be 154 further purified by column chromatography (eluent: CH_2Cl_2 then $CH_2Cl_2/MeOH$ (5/1)).

155 2,3-Dioxoindoline-5-sulfonic acid (**9**), orange-red solid, 0.14 g, 31% [37]. Mp: >300 °C. ¹H NMR 156 (400 MHz, DMSO- d_6) δ 11.14(br, s, 1H), 7.83 (dd, $J^1 = 1.4$ Hz, $J^2 = 8.1$ Hz, 1H), 7.64 (d, J = 1.4 Hz, 157 1H), 6.90 (d, J = 8.1 Hz, 1H); ¹³C NMR (100 MHz, DMSO- d_6) δ 184.64, 160.13, 151.34, 142.95, 136.03, 122.12, 117.45, 112.18. ESI-MS (100%, negative) m/z = 226 ([M-H]⁻). IR (KBr) v = 1750 159 cm^{-1} (C=O), 1621 cm^{-1} (C=O).

160 1-Ethyl-2,3-dioxoindoline-5-sulfonic acid (10), orange-red solid, 0.19 g, 37%. Mp: >300 °C. ¹H

161 NMR (400 MHz, DMSO- d_6) δ 7.87 (d, J = 8.0 Hz, 1H), 7.65 (s, 1H), 7.16 (d, J = 8.0 Hz, 1H), 3.70

162 (q, J = 6.8 Hz, 2H), 1.17 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, DMSO-*d*6) δ 183.43, 158.11,

163 150.34, 143.34, 135.15, 121.38, 116.79, 109.99, 34.49, 12.26. ESI-MS (100%, negative) m/z = 254164 ([M-H]⁻). IR (KBr) v = 1747 cm⁻¹ (C=O), 1612 cm⁻¹ (C=O).

165 1-Hexyl-2,3-dioxoindoline-5-sulfonic acid (**11**), orange-red solid, 0.37 g, 59%. Mp: >300 °C. ¹H 166 NMR (400 MHz, DMSO- d_6) δ 7.86 (dd, $J^1 = 1.6$ Hz, $J^2 = 8.0$ Hz, 1H), 7.64 (d, J = 1.6 Hz, 1H), 7.15 167 (d, J = 8.0 Hz, 1H), 3.64 (t, J = 7.2 Hz, 2H), 1.59 (m, 2H), 1.27 (m, 6H), 0.84 (t, J = 7.2 Hz, 3H). ¹³C 168 NMR (100 MHz, DMSO- d_6) δ 183.80, 158.84, 151.12, 143.95, 135.59, 121.78, 117.17, 110.51, 169 31.35, 27.15, 26.32, 22.45, 14.34. ESI-MS (100%, negative) m/z = 310 ([M-H]⁻). IR (KBr) v = 1729170 cm⁻¹ (C=O), 1614 cm⁻¹ (C=O).

171 1-Decyl-2,3-dioxoindoline-5-sulfonic acid (**12**), orange-red solid, 0.44 g, 60%. Mp: >300 °C. ¹H 172 NMR (400 MHz, DMSO- d_6) δ 7.85 (dd, $J^1 = 1.6$ Hz, $J^2 = 8.0$ Hz, 1H), 7.62 (d, J = 1.6 Hz, 1H), 7.13 173 (d, J = 8.0 Hz, 1H), 3.64 (t, J = 7.2 Hz, 2H), 1.58 (m, 2H), 1.27-1.24 (m, 14H), 0.84 (t, J = 7.2 Hz, 174 3H). ¹³C NMR (100 MHz, DMSO- d_6) δ 188.56, 163.59, 155.85, 148.83, 140.32, 126.50, 121.92, 115.23, 36.48, 34.14, 33.89, 31.94, 31.43, 27.30, 19.16. ESI-MS (100%, negative) m/z = 366176 ([M-H]⁻). IR (KBr) v = 1731 cm⁻¹ (C=O), 1614 cm⁻¹ (C=O).

177 2.5 Synthesis of dyes D1'-D4' by using 9-12 as starting materials

Concentrated sulfuric acid (15 mL, 98wt%) was added dropwisely to a solution of sulfonated
isatins (2 mmol) and thiophene (4 mmol, 337 mg) at 0°C and stirred for 3 h until the isatin derivative

- 183 2.6 General procedure for dyeing of wool, silk and nylon fabrics
- The fabric (1.0 g) was dyed at a liquor ratio of 50:1 with the dye amount at 1% owf level. Dyeing process was started at 40 °C and heated up by 1 °C/min to certain temperature (98 °C for wool and nylon, 85 °C for silk). The pH value of dye bath was controlled by AcOH/AcONa buffer solution (pH 4 for wool and silk, pH 6 for nylon). After dyeing, fabric was picked out from the dye bath, rinsed thoroughly with tap water and air-dried at room temperature.
- 189 2.7 Measurement for the dyeing properties
- 190 2.7.1 Dye exhaustion
- 191 The exhaustion of dyes was determined by spectrophotometric techniques. The dye exhaustion was192 calculated based on the following equation:

$$E(\%) = (1 - \frac{A_1}{A_0}) \times 100$$

where A_0 and A_1 are the absorbance at λ_{max} of the dye solution before and after dyeing, respectively.

194 2.7.2 Color assessment

195 Color yield of dyed fabrics was obtained from dyed samples at maximum absorption wavelength.

196 Each sample was measured three times in a different area and an average value was used. The "K/S"

197 value was calculated based on the Kubelka-Munk equation:

$$K/S = \frac{(1-R)^2}{2R}$$

where K is the adsorption coefficient, S is the scattering coefficient, and R is the reflectance of the 198 dyed sample. The color coordinates of indophenine dyes were determined on CE-7000A 199 Gretag-Macbeth computer color matching system. The color values were expressed by using CIE 200 1976 Color Space method. The coordinates used to determine color values are "L*" for lightness, 201 "*a**" for greenness (negative value) and redness (positive value), "*b**" for blueness (negative value) 202 and yellowness (positive value), " C^* " for chroma and " h° " for hue angle. 203

2.7.3 Color fastness 204

The color fastnesses to washing, rubbing and light were measured in accordance with the ISO 205 206 105-C10: 2006, ISO 105-X12: 2016 and ISO 105-B02: 2014, respectively.

3. Results and discussion 207

3.1 Synthesis and characterization of dyes D1-D4 208

The synthetic routes for water-soluble indophenine dyes are shown in Scheme 1. At first, 209 hydrophobic indophenine derivatives 5-8 were synthesized by "indophenine reaction". Subsequent 210 sulfonation of 5-8 by using concentrated sulfuric acid gave the target compounds D1-D4. Mass 211 spectra clearly showed the peak of 1/2[M-2H]²⁻ for all the four dyes, confirming the introduction of 212 two sulfonic acid groups (Figure 2). However, it is not easy to identify the exact structures of the 213 four dyes by NMR, because of the E/Z isomerization of indophenine backbone [35]. 214

To further determine the position of sulfonic acid groups in benzene rings, another synthetic route 215 was also carried out that the sulfonated isatins 9-12, prepared by sulfonation of isatins 1-4, were used 216

as the intermediates for "indophenine reaction". Since the intermediates 9-12 were structurally characterized [39], the position of $-SO_3H$ in **D1'-D4'** was definitely confirmed at the *para*-position to the *N* atom. Although the mass spectra of **D1'-D4'** were the same as that of **D1-D4**, proton NMR spectra showed big difference between **D1'-D4'** and **D1-D4** (**Figure S1** and **S2**). Considering the difference of ground-state electron cloud density distributions (**Figure S4**), the position of $-SO_3H$ in **D1-D4** were suggested mainly located at the *meta*-position rather than *para*-position to the *N* atom (detailed analysis is in S.I.).

The synthesized four dyes exhibited good hydrophilicity. **D1-D4** could not dissolve in CHCl₃, Et₂O, toluene, *etc.*, but had moderate to good solubility in water, MeOH, EtOH, DMSO and DMF. As shown in **Table 1**, the solubility of dyes in water accorded with the weight ratio of sulfonic acid groups. The introduction of alkyl chains in **D2-D4** largely decreased the weight ratio of sulfonic acid groups. As a result, the solubility decreased from 135 g/L for **D1** to less than 20 g/L for **D4**. In fact, we found that solution of **D4** in water was very instable that dyes would gradually precipitate in several hours.







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Scheme 1 Synthetic routes for dyes D1-D4 and D1'-D4'





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Table 1 Weight ratio of $-SO_3H$ in dye molecule, solubility and T_d data of **D1-D7**

	D1	D2	D3	D4	D5	D6	D7
Molecular weight/(g/mol)	586.64	642.74	754.96	866.27	637.68	451.45	669.21
Weight ratio of -SO ₃ H	0.28	0.25	0.21	0.19	0.25 ^a	0.18	0.24
Solubility/(g/L) ^b	135	130	85	< 20	135	<50	120
$T_{\rm d}$ /°C	331	323	306	290	456	220	318

^a commercial dyes are usually in the form of sodium salt, data here are calculated in the form of sulfonic acid group;
^b in water at 25 °C.

241

The thermal stabilities of synthesized dyes were evaluated by TGA technique. Generally, planar 242 molecular structure enhances π - π stacked interaction leading to high thermal stability for the dyes, 243 244 and is likely affected by electronic and steric effects. Figure 3 shows the TGA thermograms of D1-D4 as well as three reference dyes D5-D7, and the corresponding data are listed in Table 1. The 245 synthesized indophenine dyes exhibited thermal degradation temperature within the range of 246 290 °C~331 °C. The T_d values of the four synthesized dyes were in the order of D1>D2>D3>D4, 247 clearly indicated the important role of alkyl chains. The alkyl chains could rotate out of the plane of 248 the quinoidal backbone, leading to reduced tendency toward self-aggregation. As a result, $T_{\rm d}$ was 249

lowered accordingly, which was more obvious in D4 with two decyl groups. When compared with 250 the commercial dyes, the T_d values of **D1-D4** were lower than that of C.I. Acid Blue 113 (**D5**). This 251 might be caused by the larger π -conjugation system along the *bis*-azo linkage possessed by **D5**. 252 Besides, the tendency to be diradicaloid state under high temperature for indophenine quinoidal 253 heterocyclic structure might also have negative effect on the T_d values of **D1-D4** [29]. In contrast, the 254 higher T_d values of **D1-D4** than that of C.I. Acid Blue 40 (**D6**) should be caused by the relatively low 255 molecular weight and rotatable phenyl group in **D6** which might depress the tendency to aggregate. 256 Nevertheless, since the temperature in the dyeing and finishing process was usually less than 300 °C 257 [2], the synthesized dyes were confirmed to have enough thermal stability for use as textile dyes [8, 258 18]. 259

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Figure 3 Thermogravimetric analysis of D1-D7

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265 *3.2 DFT calculations*

Density functional theory (DFT) calculations were performed to further well understand the molecular geometries and electronic structures for the four designed dyestuffs [40]. Their optimized ground state geometry and the energy information were calculated by DFT/B3LYP method with 6-311g (d, p) basis set. To simplify the discussion, only *all-trans* conformation for **D1-D4** was used here. The results are shown in **Figure 4** and the collected data are summarized in **Table 2**.

The side view of the optimized ground state geometry showed highly planar quinoidal backbone 271 for indophenine dyes **D1-D4**, as observed. The high coplanarity could be further concluded from the 272 calculation for the sum of associated three bond angles or for the dihedral angles (Table S1). Hence, 273 large intermolecular interactions between dye and fiber would generate, and better wet fastness 274 property for the designed dyes was expected. The alkyl chains in D2-D4 extended outward 275 accompanied by a certain degree of inclination. Thus, intermolecular interactions could be fine-tuned 276 by controlling the length of alkyl chain. The HOMO/LUMO electron cloud density distributions for 277 **D1-D4** were mainly delocalized over the quinoidal π -conjugation system with little contribution from 278 alkyl chains or sulfonic acid groups, which was very similar with non-sulfonated indophenine 279 backbone [34]. For **D2-D4**, the HOMO/LUMO energy levels increased simultaneously as the 280 extension of alkyl chains. As a result, the bandgap had almost no change and the calculated 281 absorption maxima were the same (Figure S5). 282

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Side view

HOMO orbital

LUMO orbital





Figure 4 Optimized molecular geometries and HOMO/LUMO electron cloud density distributions for D1-D4

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Table 2Summarized calculated data for D1-D4

Dye	E/a.u.	Dipole moment/Debye	HOMO/eV	LUMO/eV	Bandgap/eV ^a	$\lambda_{\rm max}/{\rm nm}^{\rm b}$
D1	-3227.3174	0.0006	-6.2028	-4.2548	1.9480	615
D2	-3384.6046	0.0006	-6.1133	-4.1579	1.9554	601
D3	-3699.2111	0.0004	-6.0891	-4.1343	1.9591	601
D4	-4013.7909	0.0004	-6.0795	-4.1250	1.9545	601

287 ^a Bandgap = LUMO - HOMO; ^b in vacuum.

288

289 *3.3 Absorption properties*

The absorption spectra of **D1-D4** were recorded in DMSO, DMF, EtOH, MeOH and H₂O at room 290 temperature. As shown in Figure 5, only one major absorption peak was recognized in the visible 291 region with full width at half maximum (FWHM) values of 127-178 nm for all dyes (Table 3). The 292 absorption maxima of **D1-D4** were in the range of 634~652 nm and were very close in the same 293 organic solvent, evidently proving that the quinoidal π -conjugation backbone played a leading role in 294 UV-vis absorption properties. Moreover, the absorption spectra in water for dyes D1-D4 displayed 295 large hypsochromic shift with respect to that in organic solvents, associated with their purplish blue 296 color in water other than pure blue in organic solvent. Besides, the molar extinction coefficient in 297 water was relatively lower than that in organic solvent. This result indicated that these dyes might 298 aggregate in water, similar with the situation observed for **D5** with relatively large π -conjugation 299 system among the three reference dyes (Table S2) [5, 6]. The alkyl chains had little effect on the 300 absorption maxima of **D1-D4** in organic solvents which matched the theoretical calculation results. 301 However, it was found that the absorption maxima in water blue-shifted from 569 nm to 554 nm as 302 the increase of the alkyl chain length from ethyl to decyl, as a result of the increased aggregation 303 tendency. 304

As shown in **Figure S7**, the absorption spectra of **D1-D4** in water with different pH values were also measured. It was found that the four indophenine dyes showed good stability at weak acid to basic conditions, thus making them suitable for dyeing of fabrics under acid or neutral conditions. The decreased absorbance and slightly blue-shifted maximum absorption wavelength for **D1-D3** at strong acid condition (pH < 2) might be caused by further aggregation resulted from the protonation of nitrogen atoms.



Journal Pre-proof											
	FWHM/nm ^e	158	148	143	143	160	127				
	$\lambda_{\rm max}/{\rm nm}$	652	648	638	634	624	569				
D2	$\epsilon/(L \cdot mol^{-1}cm^{-1})$	29873	35563	32010	34735	-	24935				
	FWHM/nm	163	161	146	149	163	121				
	$\lambda_{\rm max}/{\rm nm}$	651	648	639	634	629	567				
D3	$\epsilon/(L \cdot mol^{-1}cm^{-1})$	30559	35308	38014	36437	-	25634				
	FWHM/nm	161	168	153	152	160	134				
	$\lambda_{\rm max}/{\rm nm}$	649	647	638	636	631	554				
D4	$\epsilon/(L \cdot mol^{-1} cm^{-1})$	30577	35208	38827	40420	-	25717				
	FWHM/nm	160	162	151	146	178	145				

^a the concentration of the dye solution is 2 × 10⁻⁵ mol/L; ^b 1/1 in volume ratio; ^c maximum absorption wavelength; ^d
 molar extinction coefficient; ^e full widths at half maximum.

321

322 *3.4 Dyeing properties*

323 *3.4.1 Dye exhaustion and color assessment*

The synthesized dyes **D1-D4** were applied to colorate wool, silk and nylon fabrics according to the procedure depicted in experimental section and compared with the three reference dyes **D5-D7**. To obtain the best dyeing performance, several dyeing parameters including dyeing temperature, pH

value of dye bath, liquor ratio and salt effect, had been screened at first (Table S3-S10). It was found
that the dyeing temperature and pH value of dye bath for these dyes were mainly decided by the fiber
other than dyestuffs. And the variation of liquor ratio and addition of salt seemed to have little effect
on the dyeing performance of D1-D3. For D4, however, the low liquor ratio value and the addition of
salt would bring about several problems, such as decreased levelness, low exhaustion, which might
be caused by its low solubility.

333

334

 Table 4
 Dye exhaustion and color parameters of dyed fabrics for dyes D1-D7^a

		<i>E</i> /% ^b	$\lambda_{\rm max}/{\rm nm}^{\rm c}$	K/S	L*	<i>a</i> *	b^*	<i>C</i> *	h°
	D1	>99	590	8.1	35.53	-4.93	-11.29	12.32	246.39
	D2	>99	590	20.0	26.78	4.06	-25.14	25.47	279.16
	D3	>99	590	19.7	26.29	6.10	-27.66	28.33	282.44
Wool	D4	>99	590	13.8	25.39	4.81	-22.10	22.62	282.28
	D5	>99	590	20.4	18.66	3.82	-13.88	14.40	285.38
	D6	>99	630	17.1	32.28	-12.55	-26.22	29.07	244.42
	D7	>99	640	26.5	47.09	-38.28	-21.42	43.87	209.23
	D1	>99	590	8.8	37.82	3.68	-22.95	23.25	279.11
	D2	>99	600	12.7	32.19	10.88	-35.22	36.87	287.17
C ;11 ₇	D3	98.5	620	10.2	31.16	6.25	-35.25	35.80	280.06
SIIK	D4	98.7	610	10.8	32.42	6.15	-33.96	34.51	280.26
	D5	97.1	590	8.3	33.45	2.88	-24.84	25.00	276.62
	D6	98.7	630	5.3	50.71	-15.22	-27.18	31.15	240.74

	Journal Pre-proof												
	D7	99.0	640	13.0	59.61	-37.02	-26.23	45.37	215.31				
	D1	93.4	650	21.3	25.48	-1.40	-21.57	21.61	266.29				
	D2	>99	650	24.9	24.66	5.17	-29.23	29.68	280.02				
	D3	>99	650	25.0	26.65	8.08	-35.68	36.58	282.76				
Nylon	D4	>99	650	25.9	24.89	7.21	-33.55	34.31	282.12				
	D5	98.3	620	21.9	22.66	0.85	-22.06	22.08	272.21				
	D6	87.8	640	15.2	37.21	-14.08	-30.21	33.33	245.00				
	D7 ^d	>99	630	25.4	47.25	-31.26	-31.93	44.69	225.61				

^a Dyeing condition: for wool, 1% owf, pH 4, 98 °C; for silk, 1% owf, pH 4, 85 °C; for nylon, 1% owf, pH 6, 98 °C;
^b Exhaustion; ^c Data collected from *K/S* curves; ^d Dyeing at pH 5.

337

As shown in Table 5, most of the fabrics dyed with D1-D4 at the optimized dyeing conditions 338 displayed blue shade with satisfactory levelness, except for the dull gray wool fabric dyed with D1. 339 The data for the dye exhaustions and color parameters of dyed fabrics were collected in Table 4. In 340 term of dye exhaustion, all the indophenine dyes showed good to excellent exhaustion values, 341 342 indicated that the synthesized dyes based on indophenine backbone had good affinity with wool, silk and nylon fibers. However, there existed remarkable differences in color depth value for the dyed 343 fabrics. Generally, fabrics dyed with **D1** showed the lowest K/S values, which might due to the low 344 coloring strength of **D1**, as demonstrated in the *K/S* curves (Figure S8). Fabrics dyed with **D4** also 345 showed relatively lower K/S values than that dyed with D2 and D3, probably due to the aggregation 346 of **D4** on fibers. This meant that suitable alkyl chains were significant for improving the color depth. 347 Outstandingly, K/S values of fabrics dyed with D2 and D3 were as high as that dyed with commercial 348

349 dyes, indicating their potential practical application as acid dyes.



351



Table 5Images of fabric samples dyed with D1-D7 at 1% owf level

- -

353 *3.4.2 Dyeing rate*

As shown in Figure 6, the dyeing rate curves of indophenine dyes D1-D4 as well as the 354 commercial dyes **D5-D7** for dyeing of wool, silk and nylon fabrics were described by collecting the 355 exhaustion data at certain dyeing time. In all cases, the synthesized indophenine dyes D1-D4 showed 356 much lower dyeing rates than the commercial dyes D5-D7. This meant that the high molecular 357 planarity of indophenine backbone might cause large dye-dye interactions so that more energy was 358 needed to permit the dye molecules transfer to fiber surface and inside. The relatively low dyeing 359 360 rate allowed the good levelness performance without addition of extra leveling agents [2]. Among the four indophenine dyes, D1 and D4 showed lower dyeing rates than D2 and D3. For dye D1 361

without substituents, this dyestuff might form inner-salt because of the coexistence of secondary amino groups and sulfonic acid groups. And for **D4**, the too long alkyl chains resulting in low water-solubility should be responsible for the low dyeing rate. Combined with aforementioned data of dyeing performance, alkyl chains with suitable length seemed to be necessary to fine tune the dye-dye and dye-fiber interaction. Specifically, **D3** with two hexyl groups exhibited the highest dyeing rate among the four synthesized dyes.





374 Dyeing condition: for wool, pH 4, 98 °C; for silk, pH 4, 85 °C; for nylon, pH 6, 98 °C (D7, pH 5)
375 Figure 6 Dyeing rate curves for wool (a), silk (b) and nylon (c) with D1-D7 at 1% owf level
376

377 *3.4.3 Effect of dye concentration*

The effects of dye concentration on the K/S values at the maximum absorption wavelength and dye 378 exhaustions were studied and the results were shown in Figure 7 and Table S11-S13. Generally, the 379 dyes exhibited good build-up properties with low dye concentration of less than 1% owf. As the dye 380 concentration increasing, the dye exhaustion could be observed with a gradual decline, indicating the 381 saturation of dye molecules on the fibers. As a result, K/S values no longer continued to increase 382 substantially. In all cases, D2 and D3 displayed much better build-up properties than D1 and D4, 383 especially in dyeing of wool fabrics where D1 and D4 showed low coloring strength and dye 384 exhaustions. To our delight, **D2** and **D3** also showed good build-up properties that were comparable 385 with commercial dyes. In case of dyeing of nylon, fabrics dyed with D2 and D3 could have higher 386 *K*/*S* values than that dyed with **D5-D7**, making it possible for deep dyeing with indophenine dyes. 387

388



389



390

Figure 7 Effect of dye concentration on *K/S* value for **D1-D7** dyeing of wool (a), silk (b) and nylon (c) fabrics

392

393 *3.4.4 Color fastness*

The color fastnesses of fabrics dyed with the indophenine dyes D1-D4 were evaluated and 394 compared with the commercial dyes D5-D7. The fastness data were summarized in Table 6. All 395 fabrics dyed with the indophenine dyes **D1-D4** showed moderate to excellent washing and rubbing 396 fastnesses, exactly indicating the positive influence of the quinoidal coplanarity of indophenine 397 backbone. Fabrics dyed with D4 were found to have relatively lower washing and rubbing fastnesses 398 than that dyed with the other three indophenine dyes. This might be due to the large dye molecular 399 size and low ratio of sulfonic acid groups for **D4** that making massive dye molecules aggregated on 400 the surface of fiber. Besides, it was noted that the staining on cotton could be remarkably eliminated 401 by increasing the alkyl chain length. The substantivity of indophenine dyes to cotton fiber also 402 promoted us to investigate the dyeing performance on cotton fabrics. However, all the low dye 403 404 exhaustions, low K/S values and wet fastness of dyed fabrics indicated the unfeasibility of indophenine dyes as the dyeing materials for cotton fabrics (Table S14 and S15). This phenomenon 405

was similar with triphendioxazine-based phosphorus containing acid dye that also had large and planar π -conjugation system, as reported in literature [17]. Among the four indophenine dyes, **D2** and **D3** exhibited the best fastness properties, and even better fastness level than the commercial dyes in term of washing fastness. The light fastness of fabrics dyed with the indophenine dyes showed relatively poor degrees, which were equal to the level for the triphenylmethane dye **D7** [41]. The poor light fastnesses for indophenine dyes must be due to the instability of indophenine backbone under irradiation [34].

413

414

 Table 6
 Color fastness data of wool/silk/nylon fabrics dyed with D1-D7

		Washing		Rub	Rubbing				
Dye	Change Staining Cotton Wool/Silk/Nylon		Staining Cotton Wool/Silk/Nylon		Wet	- Light			
D1	4/3/5 ^a	3-4/2-3/4-5	5/5/5	4-5/4/5	4/3/5	3/2-3/1-2			
D2	4-5/3-4/5	3-4/3/5	5/5/5	4-5/4/5	4/3/5	2-3/2-3/1-2			
D3	5/4/5	5/4/5	5/4-5/4-5	4-5/4-5/5	4/3-4/5	2-3/2/1-2			
D3 ^b	5/4-5/5	5/5/5	5/4-5/5	4-5/5/5	3-4/4-5/5	2/2/1-2			
D3 ^c	4-5/3/4-5	3-4/3-4/4	5/3/3-4	3-4/4-5/3	2/3/2	4/3-4/2			
D4	4/3-4/4-5	5/5/5	5/4/5	3/4/3	2-3/4/3	2-3/2/1			
D5	4-5/3/4	4/2-3/5	5/2-3/3	4-5/5/5	4/4/5	6-7/5-6/6-7			
D6	1-2/1/2-3	2/3/4	1-2/2-3/2	4-5/4-5/5	4/4/4-5	6-7/6-7/6-7			
D7	3/1/4	3/4/3-4	2-3/1/3-4	4/5/4-5	3/3-4/4	1-2/2/1			

^a The data listed in table are in the order of wool/silk/nylon; ^b Fabrics dyed with **D3** at 0.5% owf level; ^c Fabrics

416 dyed with **D3** at 2% owf level.

417

418 4. Conclusion

In summary, we have designed and synthesized four new water-soluble indophenine dyes D1-D4 419 that bearing two alkyl chains with different lengths by sulfonation of hydrophobic indophenine 420 derivatives. The sulfonic acid groups on indophenine backbone were confirmed to mainly locate at 421 the *meta*-position to the N atom. The introduction of sulfonic acid groups have made the indophenine 422 dyes dissolve well in water with solubility values in the range of 20~135 g/L. Besides, the good 423 thermal and acid-base stabilities have made these dyes suitable for coloration of textiles under acid 424 425 or neutral conditions. UV-vis absorption spectra of these blue dyes showed the maximum absorption wavelength in the range of 634~652 nm in organic solvent and rather blue-shifted values in the range 426 of 554~569 nm in water. 427

The synthesized four indophenine dyes have been well applied into dyeing of wool, silk and nylon 428 fabrics under weak acid or neutral conditions, indicating their good affinity with these fibers. In 429 some cases, the designed indophenine dyes exhibited even better dyeing performance than the 430 mentioned commercial dyes, in terms of exhaustion, build-up and wet fastness. Study of 431 structure-property relationship indicated that suitable alkyl chains were significant to fine-tune the 432 dye-dye and dye-fiber intermolecular interactions. As a result, D3 with two hexyl groups showed the 433 best overall dyeing performance among the four indophenine dyes. Therefore, the above results 434 demonstrated that the introduction of rigid quinoidal heterocyclic structure with high coplanarity as 435 chromophore backbone is an efficient method for the design of high-performance acid dyestuffs. 436

437	Further	rational	molecular	design	for	this	family	of	indophenine	dyes	to	improve	the	dyeing
438	perform	ance is o	n going nov	v in our	grou	ıp.								

439

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444

445 Appendix A. Supplementary data

446 For supplementary data related to this article, see supplementary information.

447

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539

Highlights

- Water-soluble indophenine dyes were designed and synthesized.
- Sulfonic acid group was mainly located at the *meta*-position to the *N* atom.
- The dyes showed good thermal stability and acid-base stability.
- The dyes could offer dark blue shade on wool, silk and nylon fabrics with high exhaustion.
- Fabrics dyed with indophenine dyes displayed excellent wet fastness.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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