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## Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colorless luminescent solar concentrators (LSCs)

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ARTICLE INFO	A B S T R A C T
Keywords:	New luminophores having different aryl nuclei and propynones moieties have been obtained via Sonogashira
Luminescent solar concentrator Organic dye Solvatochromism	reactions. Their optical properties were evaluated and indicated that carbonyl groups are responsible for sig- nificant bathochromic effects and high Stokes shifts. The insertion of -OMe groups on the central benzene unit
Sonogashira reaction	methacrylate) (PCMA) film and connected to a PV cell.

#### 1. Introduction

Climate changes due to pollution, together with the continuous increase in energy demand, have pushed research towards the use of renewable sources such as solar energy which is free and ubiquitous, and which utilization does not imply carbon dioxide emissions in the atmosphere. The exploitation of solar energy can take place by means of photo-thermal, photochemical or photovoltaic technology. The field of greatest interest concerns the photovoltaic (PV) sector, which regards with direct conversion of electromagnetic radiation into electrical energy. Solar cells produce a quantity of electrical energy, proportional to the total power of the absorbed light [1]. Hence, if the intensity of the incident light is increased, a linear response in energy production will be observed: this is the principle on which geometric solar concentrators are based [2]. However, this technology has some disadvantages such as a low efficiency in diffused light conditions and the need of a good system of dispersion of excess heat due to unconverted energy [3].

To compensate for the defects of optical concentrators, luminescent solar concentrators (LSCs) were developed [4]. Since 1982 when Hermann used for the first time this term [5], the literature on LSCs has been rapidly enriched with publications [6–11] and industrial patents [12–16]. LSCs are optical devices consisting of a polymeric or glass matrix and a suitable dye dispersed within the matrix itself. The dye has the function of absorbing the incident solar radiation and re-emitting light radiation at longer wavelengths by fluorescence. The emitted light is trapped within the material and concentrated towards a solar cell

on the edge of the collector thus increasing the efficiency of the system.

Fluorophores are the driving force for light concentration in LSCs cells. An effective luminophore must meet different requirements: broad spectral absorption, good matching between the dye emitted spectrum and the external quantum efficiency of the PV-cell (generally in the red zone), large Stokes shift (no or low overlap in absorption and emission spectra), high luminescent efficiency (quantum yield, QY) and thermaland photo-stability. Different luminophores have been investigated: quantum dots [17], lanthanide-based materials [18] and organic dyes [19], *i.e.* organic molecules featured by an extended planar  $\pi$ -system. Respect to the two first classes of compounds, organic dyes are usually less toxic and their optical properties can be modulated by changing portions of the carbon backbone or introducing specific functional groups. Dyes proposed for LSCs applications are coumarins, rhodamines, pyrromethane 580, naphthalimides, perylenebisimides, bipyridines, dicarbocyanins, dicyanomethylenes, oxazines, and phthalocyanines [20-33]. Among all these classes, only a very limited number of dyes have resulted in being suitable for LSCs. Therefore, a continuous investigation towards really efficient luminophores is in progress. In this context, the development of a simple synthetic methodology for obtaining  $\pi$ -conjugated variously functionalized systems could pave the way to new luminophores. Moreover, the application of LSC as architectural windows has also triggered interest in visible transparent fluorophores, which were found to provide acceptable optical efficiencies with a negligible degree of colored tinting [34]. Notwithstanding this exciting approach to harvesting solar energy for the building integrated

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photovoltaics, challenges are still open to enhance the ultimate LSC optical efficiency [10].

Here we report our principal results regarding Sonogashira based synthesis of new bis[1-(thiophenyl)propynones] derivatives and the evaluation of their optical properties also in terms of transparent solar collectors for PV.

#### 2. Experimental section

#### 2.1. Materials and apparatus

Solvents were purified by conventional methods, distilled and stored over activated molecular sieves under argon. Starting substrates thiophene-2-carbonyl chloride (4a), 3-methylthiophene-2-carbonyl chloride (4b) and 3-chlorothiophene-2-carbonyl chloride (4c) were purchased from Sigma Aldrich and used as received. All the other chemicals were purchased from commercial sources and used as received without purification. All the operations under inert atmosphere were carried out using standard Schlenk techniques and employing dried nitrogen. For all reactions, conversion was monitored by thin-laver chromatography (TLC) analysis on pre-coated silica gel plates ALU-GRAM® Xtra SIL G/UV254 (0.2 mm) purchased from VWR Macherev-Nagel. Column chromatographies were performed with Fluka silica gel, pore size 60 Å, 70-230 mesh, 63-200 µm. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> solution with a Bruker Avance DRX 400 spectrometer, operating at a frequency of 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C, using the residual solvent peak as internal reference; chemical shifts ( $\delta$ ) values are given in parts per million (ppm) and coupling constants (J) in Hertz. Mass spectra were obtained with an Applied Biosystems-MDS Sciex API 4000 triple quadrupole mass spectrometer (Concord, Ont., Canada), equipped with a Turbo-V ion-spray (TIS) source. Elemental analyses were performed on a Elementar Vario Micro Cube CHN-analyzer.

#### 2.2. Synthesis of bis[1-(thiophenyl)propynone] dyes

General procedure: in a typical run, diethynylarene (1.0 mmol), thiophene acid chloride (2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2 mol%) and Et<sub>3</sub>N (20 mL) were mixed together in a 50 mL two-necked round bottom flask. The resulting mixture was left under stirring for 28 h at 50 °C, then it was cooled to room temperature, hydrolyzed with saturated ammonium chloride solution (20 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuum. All the crude products were purified through column chromatography on silica gel and characterized with <sup>1</sup>H NMR, <sup>13</sup>C NMR, LC-MS and elemental analysis techniques.

### 2.2.1. 3,3'-(1,4-Phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (1a)

According to the general procedure, 1,4-diethynylbenzene (3) (126 mg, 1.0 mmol), thiophene-2-carbonyl chloride (4a) (367 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CHCl<sub>3</sub> 1:1), giving 288 mg (yield 83%) of 3,3<sup>-</sup>(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (1a) as yellow solid. Mp: 208–210 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.19 (2H, dd, J = 4.8, 3.8 Hz); 7.68 (4H, s); 7.75 (2H, dd, J = 4.8, 1.2 Hz); 8.00 (2H, dd, J = 3.8, 1.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 88.53; 89.74; 122.30; 128.46; 133.05 (2C); 135.34; 135.70; 144.66; 169.35. LC-MS APCI (+): calcd for C<sub>20</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub>: C, 69.34; H, 2.91; S, 18.51; found: C, 69.55; H, 2.86; S, 18.52.

### 2.2.2. 3,3'-(1,4-Phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1one) (1b)

According to the general procedure, 1,4-diethynylbenzene (3) (126

mg, 1.0 mmol), 3-methylthiophene-2-carbonyl chloride (**4b**) (402 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:5), giving 277 mg (yield 74%) of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one)

(1b) as yellow solid. Mp: 195–198 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 2.66 (6H, s); 6.98 (2H, d, J = 4.4 Hz); 7.56 (2H, d, J = 4.4 Hz); 7.66 (4H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 16.67; 89.51; 90.06; 122.35; 132.86 (2C); 132.97; 133.37; 137.62; 146.56; 169.41. LC-MS APCI (+): calcd for C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: 374.04; found *m*/*z* [M+H]<sup>+</sup>: 375.1. Anal. calcd for C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 70.56; H, 3.77; S, 17.13; found: C, 70.49; H, 3.82; S, 17.13.

# 2.2.3. 3,3'-(1,4-Phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (1c)

According to the general procedure, 1,4-diethynylbenzene (3) (126 mg, 1.0 mmol), 3-chlorothiophene-2-carbonyl chloride (4c) (453 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:5), giving 208 mg (yield 50%) of 3,3'-(1,4-phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (1c) as light yellow solid. Mp: 215–218 °C.<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 7.39 (2H, d, J = 5.2 Hz); 7.89 (4H, s); 8.25 (2H, d, J = 5.2 Hz). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 89.38; 91.90; 122.05; 130.90; 131.94; 133.87 (2C); 135.99; 136.76; 167.09. LC-MS APCI (+): calcd for C<sub>20</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 413.93; found *m*/*z* [M+H]<sup>+</sup>: 415.9. Anal. calcd for C<sub>20</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 57.84; H, 1.94; S, 15.44; found: C, 58.02; H, 1.89; S, 15.43.

# 2.2.4. 3,3'-(1,4-Phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (1d)

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 4-phenylthiophene-2-carbonyl chloride (**4d**) (557 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:5), giving 409 mg (yield 82%) of 3,3'-(1,4-phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**) as light yellow solid. Mp: 182–185 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.33–7.36 (2H, m); 7.41–7.45 (4H, m); 7.58–7.60 (4H, m); 7.71 (4H, s); 7.83 (2H, d, J = 1.6 Hz); 8.21 (2H, d, J = 1.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 88.53; 90.08; 122.29; 126.40 (2C); 128.09; 129.08 (2C); 130.19; 133.08 (2C); 133.51; 134.44; 143.82; 144.97; 169.26. LC-MS APCI (+): calcd for C<sub>32</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub>: 498.07; found *m*/*z* [M+H]<sup>+</sup>: 499.1. Anal. calcd for C<sub>32</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub>: C, 77.08; H, 3.64; S, 12.86; found: C, 77.15; H, 3.59; S, 12.86.

# 2.2.5. 3,3'-(1,4-Phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (1e)

According to the general procedure, 1,4-diethynylbenzene (3) (126 mg, 1.0 mmol), 3-ethoxythiophene-2-carbonyl chloride (4e) (477 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:4), giving 252 mg (yield 58%) of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (1e) as yellow-orange solid. Mp: 216–218 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.45 (6H, t, *J* = 6.8 Hz); 4.24 (4H, q, *J* = 6.8 Hz); 6.85 (2H, d, *J* = 5.2 Hz); 7.57 (2H, d, *J* = 5.2 Hz); 7.61 (4H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 15.05; 67.80; 89.73; 89.98; 116.88 (2C); 122.67; 132.64 (2C); 134.67; 161.82; 167.59. LC-MS APCI (+): calcd for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>: 434.06; found *m*/*z* [M+H]<sup>+</sup>: 435.4. Anal. calcd for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>: C, 66.34; H, 4.18; S, 14.76; found: C, 66.09; H, 4.21; S, 14.77.

# 2.2.6. 3,3'-(1,4-Phenylene)bis(1-(benzo[b]thiophen-2-yl)prop-2-yn-1-one) (1f)

According to the general procedure, 1,4-diethynylbenzene (3) (126



**Scheme 1.** Synthetic approach to (1,4-phenylene)bis(thiophenylpropynones) dyes 1.

mg, 1.0 mmol), benzo[b]thiophene-2-carbonyl chloride (4f) (492 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:3), giving 201 mg (yield 45%) of 3,3'-(1,4-phenylene)bis(1-(benzo[b]thiophen-2-yl)prop-2-yn-1-one) (1f) as orange solid. Mp: 206–208 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 7.42–7.46 (2H, m): 7.49–7.53 (2H, m): 7.76 (4H, s): 7.89 (2H, d, J = 8.0 Hz); 7.95 (2H, d, J = 8.0 Hz); 8.27 (2H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 88.49; 90.41; 122.37; 123.16; 125.39; 126.46; 128.26; 132.97; 133.15 (2C); 138.73; 143.34; 144.07; 170.82. LC-MS APCI (+): calcd for C<sub>28</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: 446.04; found *m/z* [M+H]<sup>+</sup>: 447.2. Anal. calcd for C<sub>28</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 75.31; H, 3.16; S, 14.36; found: C, 75.55; H, 3.14; S, 14.35.

2.2.7. 3,3'-(1,4-Phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (1g)

According to the general procedure, 1,4-diethynylbenzene (3) (126 mg, 1.0 mmol), 5-chlorothiophene-2-carbonyl chloride (4g) (453 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, n-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:5), giving 324 mg (yield 78%) of 3,3'-(1,4-phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one)

(1g) as light pink solid. Mp: 255–257 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 7.05 (1H, d, *J* = 4.1 Hz); 7.69 (2H, s); 7.80 (1H, d, *J* = 4.1 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 87.83; 90.32; 122.21; 128.01; 133.09 (2C); 134.77; 141.69; 142.88; 168.25. LC-MS APCI (+): calcd for C<sub>20</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 413.93; found *m/z* [M+H]<sup>+</sup>: 415.9. Anal. calcd for C<sub>20</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 57.84; H, 1.94; S, 15.44; found: C, 58.08; H, 1.86; S, 15.44.

#### 2.2.8. 3,3'-(1,4-Phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (1h)

According to the general procedure, 1,4-diethynylbenzene (3) (126 mg, 1.0 mmol), 5-nitrothiophene-2-carbonyl chloride (4h) (479 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/AcOEt 9:1  $\rightarrow$  7:3), giving 231 mg (yield 53%) of 3,3'-(1,4-phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (1h) as yellow-orange solid. Mp: 219–221 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 7.77 (4H, s); 7.90 (2H, d, *J* = 4.2 Hz); 7.97 (2H, d, *J* = 4.2 Hz).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 87.62; 92.41; 122.03; 128.20;



Fig. 1. Chemical structure of acid chlorides chosen as coupling partner of 3 for the synthesis of (1,4-phenylene)bis(thiophenylpropynones) dyes.

132.25; 133.38 (2C); 147.41; 157.18; 168.70. LC-MS APCI (+): calcd for C<sub>20</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: 435.98; found *m/z* [M+H]<sup>+</sup>: 437.0. Anal. calcd for C20H8N2O6S2: C, 55.04; H, 1.85; N, 6.42; S, 14.69; found: C, 54.91; H, 1.92; N, 6.43; S, 14.70.

#### 2.2.9. 3,3'-([1,1'-Biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1one) (10a)

According to the general procedure, 4.4'-diethvnvl-1.1'-biphenvl (9a) (202 mg, 1.0 mmol), thiophene-2-carbonyl chloride (4a) (367 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, n-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:4), giving 321 mg (yield 76%) of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (10a) as light yellow solid. Mp: 206–208 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.19–7.21 (2H, m); 7.66 (4H, d, J = 8.4 Hz); 7.73–7.76 (6H, m); 8.02 (2H, d, J = 4.4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 87.50; 91.15; 119.73; 127.37 (2C); 128.36; 133.67 (2C); 135.05; 135.32; 142.07; 144.93; 169,62. LC-MS APCI (+): calcd for C<sub>26</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: 422.04; found *m*/*z* [M+H]<sup>+</sup>: 423.2. Anal. calcd for C<sub>26</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 73.91; H, 3.34; S, 15.18; found: C, 73.68; H, 3.35; S, 15.18.

#### 2.2.10. 3,3'-(Naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (10b)

According to the general procedure, 2,6-diethynylnaphthalene (9b) (176 mg, 1.0 mmol), thiophene-2-carbonyl chloride (4a) (367 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:4  $\rightarrow$  CH<sub>2</sub>Cl<sub>2</sub>), giving 202 mg (yield 51%) of 3.3'-(naphthalene-2.6-divl)bis(1-(thiophen-2-vl)prop-2-vn-1one) (10b) as light yellow solid. Mp: 210–213 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.19–7.22 (2H, m); 7.71 (2H, d, *J* = 8.4 Hz); 7.75 (2H, d, J = 4.4 Hz); 7.89 (2H, d, J = 8.4 Hz); 8.05 (2H, d, J = 4.4 Hz); 8.22 (2H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 87.60; 91.01; 119.43; 128.41; 128.74; 129.57; 133.14; 133.89; 135.15; 135.46, 144.89; 169.51. LC-MS APCI (+): calcd for C<sub>24</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: 396.03; found m/z [M+H]<sup>+</sup>: 397.2. Anal. calcd for C<sub>24</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: C, 72.70; H, 3.05; S, 16.17; found: C, 72.77; H, 3.09; S, 16.16.

Fable 1
Photophysical properties of (1,4-phenylene)bis(thiophenylpropynones) dyes <b>1a</b>

Compound	ε <sup>a</sup>	$\lambda_{max}^{Absb}$	$\lambda_{\max}^{Fluoc}$	SS <sup>d</sup>	$\Phi^{e}$
1a	3.8	335	443	108	0.2
1b	3.8	338	450	112	/ <sup>f</sup>
1c	3.8	339	/	/	/ <sup>g</sup>
1d	3.4	328	467	139	0.6
1e	2.5	323	507	184	0.2
1f	4.5	343	451	108	0.2
1g	5.8	340	/	/	/ <sup>g</sup>
1h	4.6	352	/	/	/ <sup>g</sup>

<sup>a</sup> Extinction coefficient (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>).

<sup>b</sup> Maximum of light absorbance (nm).

Maximum of light emission (nm).

 $SS = Stokes shift (nm) = \lambda_{max}^{Fluo} - \lambda_{max}^{Abs}$ 

e Quantum yield (%).

f Less than 0.1%.

g Not determined.

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#### Table 2

#### Photophysical properties of arylbis(thiophenylpropinones) 10a-c.

Compound	ε <sup>a</sup>	$\lambda_{max}^{Absb}$	$\lambda_{max}^{Fluoc}$	SS <sup>d</sup>	$\Phi^{e}$
10a 10b	3.8 5.3	346 346	420	74 82	/ <sup>f</sup>
10b 10c	3,4	340 397	428	82 59	7 5.8

<sup>a</sup> Extinction coefficient ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).

<sup>b</sup> Maximum of light absorbance (nm).

<sup>c</sup> Maximum of light emission (nm).

<sup>d</sup> SS = Stokes shift (nm) =  $\lambda_{max}^{Fluo}$  -  $\lambda_{max}^{Abc}$ 

e Quantum yield (%).

f Less than 0.1%.

2.2.11. 3.3'-(Naphthalene-1,4-divl)bis(1-(thiophen-2-vl)prop-2-vn-1-one) (10c)

According to the general procedure, 1,4-diethynylnaphthalene (9c) (176 mg, 1.0 mmol), thiophene-2-carbonyl chloride (4a) (367 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:4  $\rightarrow$  CH<sub>2</sub>Cl<sub>2</sub>), giving 266 mg (yield 67%) of 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1one) (10c) as yellow solid. Mp: 212–214 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.22–7.23 (2H, m); 7.73–7.76 (2H, m); 7.78 (2H, dd, J = 4.4, 1.2 Hz); 7.92 (2H, s); 8.09 (2H, dd, *J* = 4.4, 1.2 Hz); 8.44–8.48 (2H, m).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 88.39; 92.99; 120.78; 126.50; 128.56; 128.70; 131.87; 133.27; 135.13; 135.65; 144.82; 169.30. LC-MS APCI (+): calcd for C<sub>24</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: 396.03; found *m*/*z* [M+H]<sup>+</sup>: 397.2. Anal. calcd for C<sub>24</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: C, 72.70; H, 3.05; S, 16.17; found: C, 72.83; H, 3.03; S, 16.17.

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#### 2.2.12. 3,3'-(2,5-Dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2yn-1-one) (15)

According to the general procedure, 1,4-diethynyl-2,5-dimethoxybenzene (13) (186 mg, 1.0 mmol), thiophene-2-carbonyl chloride (4a) (367 mg, 2.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol) and Et<sub>3</sub>N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO<sub>2</sub>, n-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:5), giving 346 mg (vield 85%) of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-vl) prop-2-yn-1-one) (15) as yellow-green solid. Mp: 264–267 (dec.) °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 3.98 (6H, s); 7.19 (2H, s); 7.23–7.25 (2H, m); 7.78 (2H, dd, *J* = 4.9, 1.2 Hz); 8.15 (2H, dd, *J* = 3.8, 1.2 Hz).  $^{13}\mathrm{C}$  NMR (100 MHz, CDCl\_3),  $\delta$  (ppm): 56.89; 87.60; 92.59; 113.19; 116.88; 128.66; 135.78; 136.20; 145.33; 155.85; 169.08. LC-MS APCI (+): calcd for C<sub>22</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: 406.03; found m/z [M+H]<sup>+</sup>: 407.2. Anal. calcd for C<sub>22</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: C, 65.01; H, 3.47; S, 15.78; found: C, 64.83; H, 3.41; S, 15.78.

#### 2.3. Characterization

UV-Vis absorption measurements in solution were done using a PerkinElmer Lambda 650 spectrophotometer, with temperature control to within  $\pm 0.1$  °C. Fluorescence measurements in solution were performed using a Horiba Jobin Yvon FluoroLog®-3 spectrofluorometer, with temperature control to within  $\pm 0.1$  °C.

Quantum yields  $(\Phi)$  in solution are calculated according to a comparative method, involving the use of a standard with known quantum yield,  $\Phi_{ST}$  (perylene in cyclohexane,  $\Phi_{ST} = 0.94$ ; fluorescein in 0.1 M aqueous NaOH solution,  $\Phi_{ST} = 0.95$ ; quinine sulfate in 0.1 M aqueous H<sub>2</sub>SO<sub>4</sub> solution,  $\Phi_{ST} = 0.54$ ) [35]; the equation used is



Scheme 2. Acyl Sonogashira reactions between 1,4-diethynylbenzene (3) and thiophene carbonyl chlorides 4a-h.

#### Table 3

Optical properties of dimethoxy-substituted dyes 13-15

Compounds	Yield (%) <sup>a</sup>	$\epsilon^{b}$	$\lambda_{\max}^{\text{Abs c}}$	$\lambda_{max}^{Fluod}$	SS <sup>e</sup>	$\Phi^{\mathrm{f}}$
OMe	85	1.0	345	373	28	12.3
OMe	60	3.8	377	409	32	23.3
$\begin{bmatrix} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$						
OMe	85	1.9	403	471	68	19.2

<sup>a</sup> Yield of pure product.

<sup>b</sup> Extinction coefficient  $(10^4 \text{ M}^{-1} \text{ cm}^{-1})$ .

<sup>c</sup> Maximum of light absorbance (nm).

<sup>d</sup> Maximum of light emission (nm).

<sup>e</sup> SS = Stokes shift (nm) =  $\lambda_{max}^{Fluo} - \lambda_{max}^{Abs}$ .

f Quantum yield (%).

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#### Table 4

Optical properties of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl) prop-2-yn-1-one) (15) recorded in different solvents.

Solvent	$\eta^{a}$	$\epsilon^{b}$	$\lambda_{max}^{Absc}$	$\lambda_{max}^{Fluod}$	SS <sup>e</sup>	$\Phi^{\rm f}$
Toluene	1.496	2.4	401	453	52	16.1
CHCl <sub>3</sub>	1.445	4.8	403	471	68	19.2
Acetone	1.359	21.0	402	471	69	38.4
Acetonitrile	1.344	38.8	403	484	81	40.8

<sup>a</sup> Refractive index.

<sup>b</sup> Dielectric constant.

<sup>c</sup> Maximum of light absorbance (nm).

<sup>d</sup> Maximum of light emission.

<sup>e</sup> SS = Stokes shift (nm) =  $\lambda_{max}^{Fluo} - \lambda_{max}^{Abs}$ .

f Quantum yield (%).

$$\Phi_{\mathrm{x}} = \Phi_{\mathrm{ST}} \cdot \frac{\nabla_{\mathrm{x}}}{\nabla_{\mathrm{ST}}} \cdot \frac{(\eta_{\mathrm{x}})^2}{(\eta_{\mathrm{ST}})^2}$$

where  $\nabla_x$  and  $\nabla_{ST}$  are the slopes of a fluorescence area vs. absorbance plot for the dye and standard, respectively, while  $\eta_x$  and  $\eta_{ST}$  are the refractive index of the solvents used for dye and standard solutions, respectively ( $\eta_{chloroform}=1.445; \eta_{cyclohexane}=1.426; \eta_{water}=1.33).$ 

15/PCMA thin films were prepared by drop casting, *i.e.* pouring 0.8 mL chloroform solution containing 120.0 mg of the polymer and the



Scheme 3. Synthesis and optical properties of 1,4-bis(thiophen-2-ylethynyl) benzene (6).



**Fig. 2.** UV–Vis absorption (a) and emission (b) normalized spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (15) in different solvents. Sample concentration:  $1.7 \times 10^{-5}$  M for absorption spectra,  $1.0 \times 10^{-6}$  M for emission spectra; cell length: 1 cm; excitation wavelength: 335 nm.



Scheme 4. Synthetic approach to arylbis(thiophenylpropinones) 10a-c.

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**Fig. 3.**  $1.0 \times 10^{-6}$  M solutions of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) dye in different solvents (from left to right: toluene, chloroform, acetone, acetonitrile), illuminated with daylight (up photo) and irradiated with UV light at 335 nm (down photo).



**Fig. 4.** UV–Vis absorption spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in CHCl<sub>3</sub> recorded each 15 min for 6 h. Sample concentration:  $1.7 \times 10^{-5}$  M; cell length: 1 cm.

proper amount of fluorophore to obtain concentrations in the range 0.7–1 wt% on 50  $\times$  50  $\times$  3 mm optically pure glass substrate (Edmund Optics Ltd BOROFLOAT window 50  $\times$  50 TS). The glass slides were cleaned with chloroform and immerged in 6 M HCl for at least 12 h; then, they were rinsed with water, acetone and isopropanol and dried for 8 h at 120 °C. Solvent evaporation was performed on a warm hot plate (about 30 °C) and in a closed environment. The film thickness was measured by a Starrett micrometer to be 200  $\pm$  10  $\mu$ m.

The optical efficiency of the LSC was measured by using a solar simulating lamp (ORIEL® LCS-100 solar simulator 94011A S/N: 322, AM1.5G std filter: 69 mW/cm<sup>-2</sup> at 254 mm). The PV module (IXYS SLMD121H08L mono solar cell 86  $\times$  14 mm) was connected to Keysight Technologies B2900 Series Precision Source/Measure Unit. The optical efficiency  $\eta_{opt}$  was evaluated from the concentration factor C, which is the ratio between the short circuit current measured in the case of the cell over the LSC edge (I<sub>LSC</sub>) and short circuit current of the bare cell

when perpendicular to the light source ( $I_{SC}$ )

$$\eta_{opt} = \frac{I_{LSC}}{I_{SC} \cdot G}$$

where G is the geometrical factor (in our case, G = 13.3), which is the ratio between the area exposed to the light source and the collecting area.

#### 3. Results and discussion

We started our study with the synthesis of (1,4-phenylene)bis(thiophenylpropynones) 1 (Scheme 1) characterized by the presence of a benzene ring linked to thiophenyl moieties through a C $\equiv$ C-C $\equiv$ =O spacer. The synthetic strategy chosen for the preparation of these compounds consists of two main steps: the synthesis of the central diethynyl functionalized nucleus and the subsequent coupling with thiophene carbonyl chlorides (Scheme 1). Both steps are based on Sonogashira cross-coupling reactions: the first is the "classic" version of the reaction [36], the second consists of the acyl copper-free Sonogashira coupling [37,38].

In details, 1,4-diethynylbenzene (**3**) was obtained from the reaction between commercial available 1,4-dibromobenzene (**2**) and an excess of ethynyltrimethylsilane, followed by quantitative desilylation of product **5** performed with aqueous solution of NaOH (see Scheme S1 in Supporting Information). As coupling partner of 1,4-diethynylbenzene (**3**), eight different acid chlorides were chosen (Fig. 1). While compounds **4ac** were commercially available, acid chlorides **4d-4f** were easily prepared starting from the methyl esters by hydrolysis with aqueous NaOH. The obtained carboxylic acids were converted into the acid chlorides by treatment with oxalyl chloride. Analogously, chlorides **4g-h** were obtained treating the commercial corresponding acids with (COCl)<sub>2</sub> (Scheme S2).

Since it is known that decarbonyation and C=C-C=C side reactions [39,40] may occur if acid Sonogashira reactions are performed at high temperature, a preliminary cross coupling between 1,4-diethynylbenzene (3) and thiophene-2-carbonyl chloride (4a) was performed at room temperature for 28 h. The analysis of crude product indicated an almost complete conversion of the reagents but the formation of a mixture of both mono- and di-thiophene carbonyl derivatives (Scheme S3 in Supporting Information).

In order to increase the chemoselectivity of the reaction, a second run was carried out at 50 °C. In this case the total consumption of the reagents occurred and the exclusive formation of expected product **1a** was observed (yield 83%). As a consequence, the improved experimental reaction conditions (50 °C, 28 h, 1 mmol of 1,4-diethynylbenzene (**3**), 2.5 mmol of thiophene carbonyl chloride, 20 mL of Et<sub>3</sub>N, and 2 mol% of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>) were applied to the acyl Sonogashira reaction between **3** and thiophene carbonyl chlorides **4** (Scheme 2). The reactions afforded exclusively di-carbonyl compounds **1a-h** and proved amenable to acid chlorides containing both electron-donating and electron-withdrawing functionality, delivering products in good yields, regardless of the position of the functional group on the thiophene ring.

Study of the optical properties of compounds **1a-h** was undertaken in CHCl<sub>3</sub> solutions. The main results obtained are collected in Table 1, while full absorbance and fluorescence emission spectra are depicted in Figs. S1–S8 in Supporting Information.

Products **1c**, **1g** and **1h**, featured by electron-withdrawing moieties did not show fluorescence when excited at 335 nm wavelength [41-43]. On the contrary, compounds **1a,b,d,e,f** showed emission spectra with high Stokes shifts (108–168 nm), indicating low auto-absorption in solution and good potentiality as fluorophores in LSC devices. Unfortunately their quantum yields were almost negligible (less than 1%).

In order to evaluate the effect of carbonyl group on the optical properties of (1,4-phenylene)bis(thiophenylpropynones) **1**, 1,4-diethynylbenzene **3** was reacted with 2-iodothiophene **5** affording 1,4-bis



Fig. 5. Absorption and emission of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (15) in PCMA film at a concentration of 0.7 wt%.

(thiophen-2-ylethynyl)benzene 6 in good yield (Scheme 3).

A comparison between optical properties of **6** (Scheme 3 and Figure S9) and **1a** (Table 1 and Fig. S1) clearly indicated that the presence of CO determines an increase of the Stokes shift, a significant bathochromic effect in emission spectra, but also a dramatic reduction of quantum yield (0.2 *vs.* 9.9%). A similar trend had been observed [32] when we studied the photophysical features of two triphenyl amine derivatives containing ethynyl linkers to thiophene or carbonylthiophene moieties. The presence of CO involved higher Stokes shifts and increase in both absorption and emission maximum wavelengths.

Thus, with the aim to improve the optical properties, bis(thiophenylpropynones) containing nucleus with extended conjugation were synthesized (Scheme 4). Analogously to the synthetic sequence employed for the synthesis of derivatives **1a-h**, central units were prepared starting from the corresponding dibromo derivatives **7a-c**, which were coupled with trimethylsilylacetylene generating **8a-c**; subsequent desilylation step (KOH) afforded diynes **9a-c** in good yields (Scheme S4).

The optical properties of dyes **10a-c** in CHCl<sub>3</sub> solution are collected in **Table 2** and **Figs. S10–S12**. While biphenyl (**10a**) and 2,6-naphtyl (**10b**) derivatives showed optical features very similar to 3,3'-(1,4phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**) in terms of maximum absorbance and emission wavelength, 3,3'-(naphthalene-1,4diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**) showed a significant bathochromic effect ( $\lambda_{max}^{Abs} = 397$  nm for **10c**, 335 for **1a**) together with an increase of quantum yield (5.8% for **10c** vs. 0.2% for **1a**). Such results could be related to both the increasing of  $\pi$ -conjugation and to the different geometry of **10c** respect to **1a** [44].

Considering that the presence of an electron-donating group such as -OEt had determined a remarkable bathochromic effect and a very high SS value (Table 1, 1e) the syntheses of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (14) and 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (15) were carried out (Scheme S5). Central nucleus 1,4-diethynyl-2,5-dimethoxybenzene (13) was easily prepared starting from commercially available 1,4dibromo-2,5-dimethoxybenzene (11) which was coupled with ethynyltrimethylsilane affording 12 (Scheme S5, step a). After desilylation with KOH/MeOH (Scheme S5, step b), product 13 was generated in high yield. and was then successfully employed in the synthesis of 14 and 15 via Sonogashira reactions (Scheme S5, steps c-d). The optical properties in CHCl<sub>3</sub> solution of both compounds are described in Table 3 and compared with those of precursor 13 (full absorbance and fluorescence emission spectra of 13-15 are reported in Figs. S13-S15 in Supporting Information). As is evident from data collected in Table 3, wavelengths of absorption and emission maxima of the three compounds vary significantly with their structure. Indeed, going from diyne 13 to

compounds **14** and then to **15** the extension of conjugation determines a red-shift of the spectrum, but with an absorption maximum still peaked close to the near-UV region.

Moreover, the presence of CO causes an increasing of the Stokes shift from 28 to 68 nm. If we compare the optical properties of **15** with compound **1a** it is evident that the presence of -OMe group involves a clear improvement of the quantum yield, from 0.2 for **1a** to about 20% for **14** and **15**, possibly due to a restricted molecular mobility. Furthermore, since **15** appeared as a promising fluorophore for colorless solar collectors, further investigations were carried out. Notably solvatochromism analyses were performed in solvents with different polarities but refractive index ( $\eta$ ) close to that of acrylate polymers, *i.e.* the most common matrix for LSC devices (Table 4 and Figs. 2 and 3).

As it is evident, the choice of the solvent has a great influence on the photophysical properties of **15**. In particular, as polarity increases from toluene to acetonitrile, a significant enhancement of quantum yield (*i.e.* 16.1 in toluene respect to 40.8% in acetonitrile) and Stokes shift (from 52 to 81 nm) were detected. In the different solvents,  $\lambda_{max}^{Abs}$  is constant and  $\lambda_{max}^{Fluo}$  increases as polarity increases. This shift of the emission to lower energy is due to the stabilization of the (polar) excited state by the polar solvent molecules. The increase in the quantum yield with solvent polarity is related to a decrease of non-radiative decays, in agreement with the increased values of Stokes shift [45].

All solutions were also checked for stability in time: absorption spectra collected over all the range were totally super imposable over 6 h of continuous irradiation at the excitation wavelength (Fig. 4).

A preliminarily investigation of 15 as a potential fluorophore for colorless LSC was carried out by dispersing 0.7 wt% of the dye in a polymer matrix of poly(cyclohexylmethacrylate) (PCMA). PCMA is 100% amorphous, transparent and commercially available, features that make this matrix suitable for LSC applications (Fig. 5). In the PCMA film (thickness of about 200 µm), 15 showed absorption in the near-UV region with a negligible contribution in the visible range of the light spectrum (at 450 nm, about 80% of transmitted light, Fig. 5). 15 displayed an emission maximum at about 470-480 nm, in agreement with data collected in solution (Table 4). The performances of the PCMA/15 film as solar collector were determined on optically pure 50  $\times$  50  $\times$  3 mm glass by using a Si-based PV cell attached to one edge of the LSC. The data acquired followed a peculiar trend, *i.e.* optical efficiency increasing with 15 content and levelling off for concentration higher than 0.7 wt% possibly due to adverse dissipative phenomena. Notably, maximum optical efficiencies of 7.7% was obtained and resulted higher than those of previously investigated bis-azido fluorophores for colorless LSC and determined with the same laboratory setup [34].

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#### 4. Conclusion

In summary, an easy methodology for the preparation of new bis (thiophenylpropynones) based on Sonogashira cross-coupling reactions has been developed. All compounds were generated in good to high yields and were tested as organic dyes for LSCs. The presence of carbonyl functional groups determined a significant bathochromic effect in emission spectra. Moreover, increasing  $\pi$ -conjugation of thiophenyl lateral unit determined an increase in Stokes shifts up to 180 nm, thus indicating low auto-absorption in solution. Replacement of benzene ring with naphthalene nucleus involved an increment of quantum yield but best results were obtained when -OMe groups were bonded to the central benzene ring (15), with quantum yield of 19.2% and SS of 68 nm. Important solvatochromism was observed when 15 was characterized in solvents with different polarity and refractive index  $(\eta)$ , with an increase of quantum yield up to  $\sim$  41% in acetonitrile. Finally a PCMA film of 15 connected to a PV cell showed maximum optical efficiency of 7.7%, thus supporting the use of this compound as fluorophore for colorless LSC devices.

#### Declaration of competing interest

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.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.dyepig.2019.108100.

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