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## Quantitative one-pot synthesis method for industrial azo pigments with recyclable wastewater

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Most industrial azo pigments are synthesized by diazotization in one pot and then coupling in another. This two-pot process has been transformed into a one-pot method by adding granular PTFE (polytetrafluoroethylene) to a mechanically agitated aqueous mixture of NaNO<sub>2</sub>, HCl, a diazo component and a coupling component. This method avoids the step of using a base or surfactant to dissolve the coupling component. The reactions were fast and quantitative. The granular PTFE, wastewater and excess HCl were then reused 11 times without deteriorating the reaction rate and product purity. Altogether, 22 industrial pigments and 3 azo compounds were synthesized and the reaction can produce up to 22.7 g of product in the laboratory. Some reactions require less than 2 equiv of HCl and a mechanism explaining this is proposed. In addition, an *o*-nitro group effect is advanced to explain the differences in coupling reaction rates for *o*-, *m*- and *p*-nitroaniline.

### Introduction

Azo compounds are used in many fields such as printing,<sup>1</sup> paints,<sup>1</sup> color photography,<sup>2</sup> textile,<sup>3</sup> chemical research,<sup>4</sup> materials,<sup>5</sup> biopharmaceutical research,<sup>6</sup> and metallochromic indicators.<sup>7</sup> In 2010, ca 560,000 tons of industrial organic pigments were produced worldwide and 59% of that was azo pigments, valued at more than 7 billion dollars.<sup>2,8</sup> Several types of reactions are used to synthesis azo compounds including azo coupling reaction, the Mills reaction, the Wallach reaction, the reduction of azoxybenzenes, the oxidation of anilines, the dehydrogenation of arylhydrazines, and the dimerization reaction of diazonium salts.<sup>9</sup>

Azo coupling reactions are widely used for the preparation of azo pigments on an industrial scale. There are three types of coupling methods: direct coupling, indirect coupling, and the "Pendulum" technique.<sup>10</sup> In the direct coupling method, the coupling component is first dissolved in an alkaline solution. The solution is filtered and then acid is added to form a suspension, to which the diazonium compound is added. In the indirect method, a clarified acidic diazonium salt solution is introduced into a solution containing the alkaline coupling compound. In the "Pendulum" technique, a constant pH is maintained by adding a dilute NaOH solution to the coupling reaction.

All these methods require more than 1.0 equiv of base to transform the coupling components into their salts, and this base then has to be neutralized. This results in large amounts of waste brine. In some cases, surfactants are used to enhance the solubility

of the coupling component. It is estimated that the production of one ton of pigments uses 120-380 tons of water and in 2010, in just China alone, this resulted in 2.69-8.51×10<sup>7</sup> tons of wastewater.<sup>2,8,11</sup> Further few of the reactions are quantitative and the waste brine from these reactions are environmentally hazardous and toxic to aquatic life as well as being aesthetically unacceptable.<sup>12,13</sup> The treatment of these wastewaters is very costly.

Therefore many efforts have been made to make these reactions green. These have included using solid acids to replace HCl,<sup>14</sup> using HNO<sub>3</sub>(ac)/HCl(g) to replace NaNO<sub>2</sub>,<sup>15</sup> using a CO<sub>2</sub>/H<sub>2</sub>O system to synthesize the diazonium salts,<sup>16</sup> using clay catalysts like bentonite, kaolin or K10 for the diazotization reactions,<sup>17</sup> and solventless syntheses.<sup>18</sup> However, the yields for these methods are not quantitative and in some cases the products had to be purified by chromatography. In another report, a suspension of the coupling compound was achieved by simply heating the coupling compound in water but this took a long time and required two vessels, although it was claimed to be a one-pot reaction.<sup>19</sup>

In previous work, our research group has used granular PTFE to make organic solvent-mediated reactions green.<sup>20,21,22</sup> Herein, we report the application of this approach to the synthesis of azo compounds. Granular PTFE was added to a mechanically agitated aqueous mixture of a diazo component, a coupling component, HCl and NaNO<sub>2</sub> to produce a variety of azo compounds. The mother liquid was then reused in another cycle after adding 1.0 equiv of fresh HCl. The wastewater, granular PTFE and excess HCl could be recycled 11 times.

### Results and discussion

Initially the synthesis of Pigment Red 1 (Table 1, **1**) was investigated by mechanically stirring a mixture of 2-naphthol (1 g), *p*-nitroaniline (1.05 equiv), HCl (1.25 equiv), H<sub>2</sub>O (3 mL), a solution of NaNO<sub>2</sub> (1.10

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equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g) at 40 °C for 2 h (Table 1, entry 1). After filtration and drying the product, a quantitative yield of **1** was obtained. Increasing the amount of HCl to 2 equiv and lowering the reaction temperature to rt shortened the reaction time from 2 h to 5 min and still resulted in a quantitative yield (Table 1, entry 2). Further increasing the amount of HCl to 3.5 equiv did not change the performance of the reaction (Table 1, entry 3). The same was true when the amount of H<sub>2</sub>O was increased to 8 mL (Table 1, entry 4). However, when the amount of H<sub>2</sub>O was reduced to 0 mL, the reaction was incomplete (81% in 120 min) (Table 1, entry 5). Quantitative yields were also obtained in 5 min when the 2 equiv of HCl was replaced with 2 equiv of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> or HBF<sub>4</sub> (Table 1, entries 6-8). Traditionally HCl has been used in the synthesis of azo pigment, so it was chosen. Based on these results the optimal amounts of water and HCl for this reaction are 3 mL and 2 equiv respectively and the optimal temperature is rt.

Six azo products were then prepared using this one-pot procedure (Table 2, 1-6). The products were collected by simple filtration, washed with water and then dried. All the reactions were quantitative and fast (5-90 min). Some of the reaction times could be shortened by adjusting the amount of acid. For example, using 2.35 equiv of HCl to prepare **4** and **5** shortened the reaction time (Table 2, entries 8 and 10). The amount of HCl was reduced to less than 2 equiv by conducting the reactions at rt (Table 2, entries 6 and 11) or 40 °C (Table 2, entries 2 and 4). The reaction rate differences for entries 7 and 9 can be attributed to the different solubilities of acetoacetanilide (32290 mg/L) and 2',4'-dimethylacetoacetanilide (3327.9 mg/L).<sup>23</sup> Since the former is more soluble, it reacts faster.

In the classical synthesis of azo pigments, the diazotization and azo coupling reactions need two pots. The diazotization is often carried out at 0 °C and here this was done at rt, so this represents a

large energy-savings. Traditionally azo couplings are a three-step two-pot reaction but this synthesis is one-step and one-pot and therefore represents a great improvement in pot efficiency.

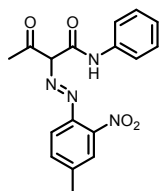
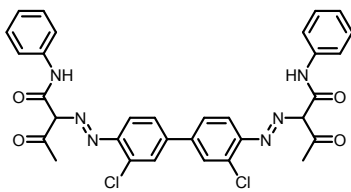
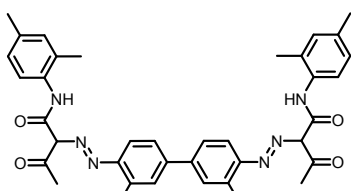
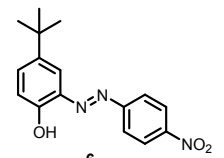
**Table 1** Optimization of the synthesis of Pigment Red 1 (**1**)<sup>a</sup>

Entry	Acid	Acid (equiv)	H <sub>2</sub> O (mL)	T (°C)	t (min)	Conversion <sup>b</sup> (%)	Isolated yield (%)
1	HCl	1.25	3	40	120	100	>99
2	HCl	2	3	rt	5	100	>99
3	HCl	3.5	3	rt	5	100	>99
4	HCl	2	8	rt	5	100	>99
5	HCl	2	0	rt	120	81	-
6	H <sub>2</sub> SO <sub>4</sub>	2	3	rt	5	100	>99
7	H <sub>3</sub> PO <sub>4</sub>	2	3	rt	5	100	>99
8	HBF <sub>4</sub>	2	3	rt	5	100	>99

<sup>a</sup>Reaction conditions: 2-naphthol (1 g), *p*-nitroaniline (1.05 equiv), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O), acid, H<sub>2</sub>O, granular PTFE (2.5 g), mechanical stirring (400 rpm). <sup>b</sup>Determined by <sup>1</sup>H NMR.

**Table 2** One-pot synthesis of azo compounds in the presence of granular PTFE<sup>a</sup>

Coupling component + Ar-NH <sub>2</sub>		HCl, NaNO <sub>2</sub>		Azo compound	
		H <sub>2</sub> O, granular PTFE			
Coupling component = 2-naphthol, acetoacetanilides, 4- <i>tert</i> -butylphenol					
Entry	Product	HCl (equiv)	T (°C)	t (min)	Isolated yield (%)
1		2	rt	5	>99
2	<b>1</b> , Pigment Red 1	1.25	40	90	>99
3		2	rt	90	>99
4	<b>2</b> , Pigment Yellow 4	1.25	40	45	>99

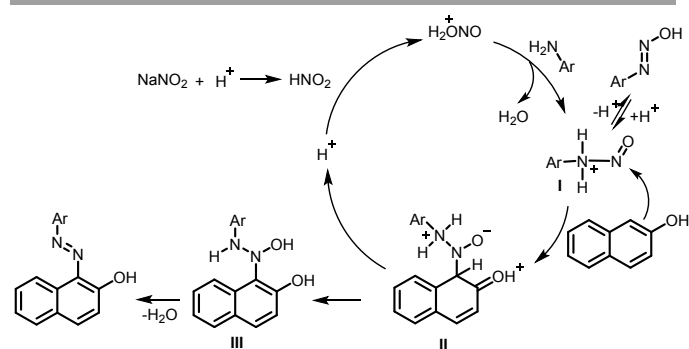
5		2	rt	40	>99				View Article Online DOI: 10.1039/C8GC03982H
6	3, Pigment Yellow 1	1.5	rt	45	>99				
7		2	rt	30	>99				
8	4, Pigment Yellow 12	2.35	rt	20	>99				
9		2	rt	45	>99				
10	5, Pigment Yellow 13	2.35	rt	20	>99				
11		1.25	rt	60	>99				

<sup>a</sup>Reaction conditions: coupling component (1 g), aromatic primary amine (1.05 equiv), HCl, H<sub>2</sub>O (3 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O), granular PTFE (2.5 g), mechanical stirring (400 rpm).

In order to save water and avoid using excess HCl, the recyclability of the reaction media in the synthesis of **3** was tested. The mother liquid, PTFE and washing water from the filtration were used in a second cycle. In addition to the reaction reagents (acetoacetanilide, 4-methyl-2-nitroaniline and NaNO<sub>2</sub>), 1.1 equiv of HCl was added to acidify NaNO<sub>2</sub> in the next cycle. The first cycle was complete in 45 min and the second cycle only needed 30 min. This procedure was repeated 11 times and quantitative yields were obtained in all cases. The reaction time was 30 min for all the cycles after the first one which is because the HCl accumulated with subsequent cycles. At the end of 11th cycle, the volume of the mother liquid and washing water was 15.5 mL.

Theoretically, more than 2 equiv of HCl are required to carry out the diazotization and coupling reactions. However, less than 2 equiv of HCl were needed for the syntheses of **1**, **2**, **3** and **6** (Table 2). A proposed mechanism for this reaction is shown in Scheme 1. First NaNO<sub>2</sub> is converted into HNO<sub>2</sub> using 1 equiv of HCl. The protonated nitrous acid then nitrosates aniline to form **I**, and **I** couples with 2-naphthol to form **II**. The deprotonation of **II** produces **III** and then a H<sub>2</sub>O molecule is eliminated to yield the final product. The proton liberated in the conversion of **II** to **III** is then used to protonate nitrous acid. As seen from the mechanism, the 1 equiv of H<sup>+</sup> liberated after the coupling reaction is reused to continue the

reaction whereas in the classical procedure this proton is not reused and has to be neutralized by 1 equiv of base.



**Scheme 1** Proposed mechanism for the synthesis of azo pigments using less than 2 equiv of HCl.

When this one-step, one-pot procedure was applied to other pigments, the reaction mixture agglomerated around the granular PTFE and the reaction was incomplete. This problem was solved by performing the one-pot reaction in two steps. First a mixture of 2-chloro-4-nitroaniline (1.05 equiv), HCl (3 equiv), H<sub>2</sub>O (3 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g) was stirred for 20 min and then 2-naphthol (1 g) was added to the reaction mixture (Table 3, entry 1). The product was collected by simple filtration,

washed with water and then dried. The reaction was quantitative. When the amount of H<sub>2</sub>O was increased from 3 to 8 mL, the reaction results were the same (Table 3, entry 2). However, when 0 mL of H<sub>2</sub>O was used (Table 3, entry 3), the reaction was incomplete (conversion 75%, 120 min). Lowering the amount of HCl from 3 equiv to 2 or 1.25 equiv also led to incomplete reactions (Table 3, entries 4 and 5).

**Table 3** Optimization of the synthesis of Pigment Red 4 (**7**)<sup>a</sup>

Entry	HCl (equiv)	H <sub>2</sub> O (mL)	T (°C)	t (min)	Conversion <sup>b</sup> (%)	Isolated yield (%)
1	3	3	rt	10	100	>99
2	3	8	rt	10	100	>99
3	3	0	rt	120	75	-
4	2	3	rt	60	71	-
5	1.25	3	rt	120	85	-

<sup>a</sup>Reaction conditions: 2-chloro-4-nitroaniline (1.05 equiv), HCl, H<sub>2</sub>O, NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g), mechanical stirring (400 rpm), 20 min; 2-naphthol (1 g). <sup>b</sup>Determined by <sup>1</sup>H NMR.

**Table 4** Effects of granular PTFE on the reaction rates<sup>a</sup>

Entry	Amount of 2-naphthol (g)	Amount of granular PTFE (g)	2-Naphthol:Granular PTFE	H <sub>2</sub> O (mL)	10 min, C <sup>b</sup> (%)	20 min, C <sup>b</sup> (%)	40 min, C <sup>b</sup> (%)	60 min, C <sup>b</sup> (%)
1	1	0.5	1:0.5	3	70	71	74	79
2	1	1.5	1:1.5	3	71	79	85	100
3	1	2.5	1:2.5	3	81	91	100	-
4	1	5	1:5	3	100	-	-	-
5	1	10	1:10	3	100	-	-	-
6	5	7.5	1:1.5	23	78	84	86	100
7	10	12	1:1.2	45	76	100	-	-
8	10	10	1:1	45	75	78	85	100
9	1	0	-	3	-	-	-	50
10	1	0	-	3	-	-	-	75

<sup>a</sup>Reaction conditions: 2-chloro-4-nitroaniline (1.05 equiv), HCl (3.0 equiv), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O), H<sub>2</sub>O and granular PTFE, mechanical stirring (400 rpm), 20 min; 2-naphthol (1 g). <sup>b</sup>Conversion, determined by <sup>1</sup>H NMR.

In the control experiments, with magnetic stirring and regular mechanical stirring and no granular PTFE, the conversions at 60 min

One major difference between our synthesis and the classical method is the use of granular PTFE in the agitated the reaction. Therefore, the effect of the ratio of substrate to granular PTFE was investigated using the synthesis of Pigment Red 4 (Table 4, **7**). First a mixture of 2-chloro-4-nitroaniline (1.05 equiv), HCl (3 equiv) in H<sub>2</sub>O (3 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE was stirred at rt for 20 min and then 2-naphthol (1 g) was added. To 1 g of 2-naphthol were added 0.5 g, 1.5 g, 2.5 g, 5 g, and 10 g of granular PTFE respectively (Table 4, entries 1-5). With 0.5 g granular PTFE (Table 4, entry 1), a yield of only 79% was achieved at 60 min. With 1.5 g granular PTFE, the reaction was over in 60 min (Table 4, entry 2) and for 2.5 g, 40 min was required (Table 4, entry 3). When 5 or 10 g granular PTFE (Table 4, entries 4-5) was used, the reactions were complete in 10 min. The reaction rate with 1.5 g granular PTFE is acceptable (2-naphthol:granular PTFE = 1:1.5).

When the amount of 2-naphthol was increased to 5 g and the granular PTFE to 7.5 g, the reaction took 60 min (Table 4, entry 6, 2-naphthol:granular PTFE = 1:1.5). When the scale of the reaction was further increased (Table 4, entry 7, 10 g of 2-naphthol, 12 g of granular PTFE; 2-naphthol:granular PTFE = 1:1.2), the reaction was complete in 20 min. If the amount of granular PTFE was reduced to 10 g, then the reaction took 60 min (Table 4, entry 8, 2-naphthol:granular PTFE = 1:1). These results show that when the reaction scale is increased from 1 to 10 g, the ratio of 2-naphthol to granular PTFE is increased from 1:1.5 to 1:1.

were 50% and 75% respectively (Table 4, entries 9 and 10). The results for the twice 10-g scale reactions (product scale: 22.7 g)

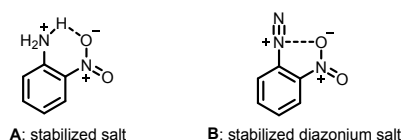
indicate the possibility that this method maybe suitable for the industrial scale up of azo pigments.

The success of this reaction is due to the large number of PTFE granules that under stirring have large momentums. Thus they can smash the water-insoluble coupling component and the insoluble pigment product. Its function is similar to the step in the classical process where coupling component in alkaline solution is converted into fine particles upon addition of acid. In the large scale preparations, the radius of the flask is larger and the granular PTFE have even higher momentums. That is why a higher ratio of 2-naphthol to granular PTFE can be used in the large scale reactions. This phenomenon has previously been observed in the aqueous synthesis of insoluble esters.<sup>20</sup>

This method was then used to synthesize 17 industrial organic pigments and 2 azo compounds (Scheme 3, products **7-25**). All of the reactions were completed within 10 to 60 min. Most of the reactions were conducted at rt with a few done at 60 °C. All the products were obtained in quantitative yields after simple filtration with no further purification. For **12** and **13**, 10 equiv of H<sub>2</sub>SO<sub>4</sub> was used because 3 equiv of HCl gave incomplete reactions.

In the synthesis of 2-naphthol-based pigments, *p*-nitroaniline and *m*-nitroaniline diazo components reacted faster than *o*-nitroaniline compounds (Scheme 3, **7-9** vs **10-13**). An explanation for this was not found in the literature<sup>10,24</sup> but we believe that the negatively charged oxygen atom on the *o*-nitro group plays an important role. This effect is shown in Scheme 2. The nitro group forms a stabilized salt (Scheme 2, **A**) that makes the amino group less nucleophilic toward the nitrosating agent. In addition, the negatively charged

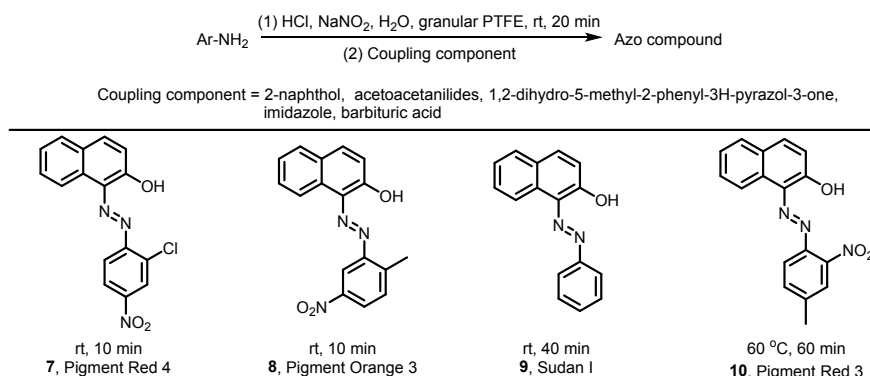
oxygen atom can stabilize the neighboring positively charged diazonium salt (Scheme 2, **B**). This makes the diazonium salt less electrophilic toward the coupling component. We call this the *o*-nitro group effect. This effect can also be used to explain the classical synthesis with *o*-nitroaniline as the diazo component where the coupling reaction took 19 h, whereas *p*-nitroaniline only took 19 min.<sup>25,26</sup>



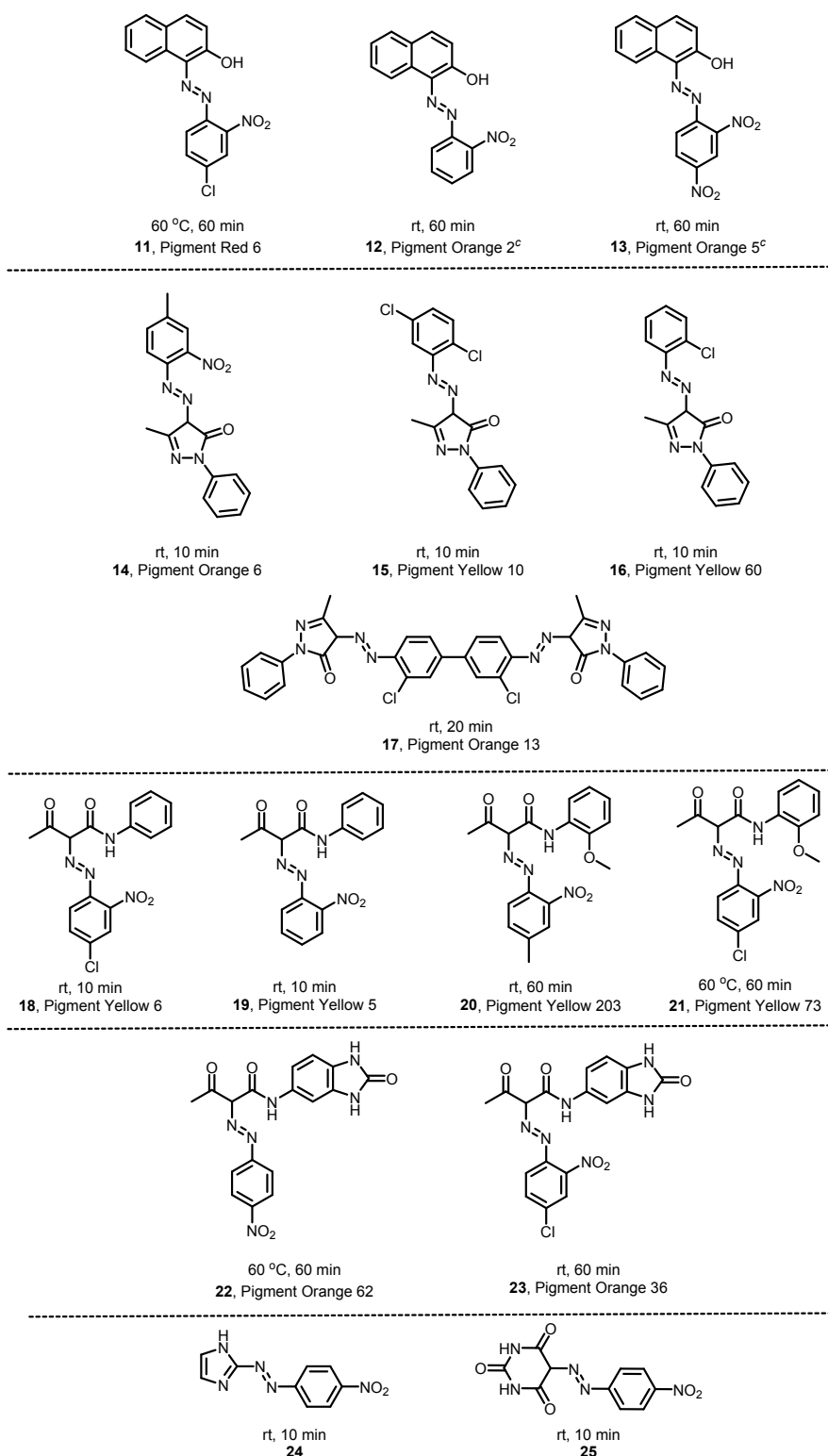
**Scheme 2** *o*-Nitro group effect.

This *o*-nitro group effect was not observed for the four pyrazolone-based pigments (Scheme 3, **14-17**). All these reactions were carried out at rt and were fast (10-20 min). This is probably because the pyrazolone ring is less hindered and more nucleophilic than the 2-naphthol ring.

A comparison of the reaction rates for the six acetoacetanilide-based pigments (Scheme 3, **18-23**) shows that the solubility of the coupling component affects the reaction rate. Higher diazo component solubilities resulted in higher reaction rates (acetoacetanilide: 32290 mg/L (10 min), *o*-acetoacetanilide: 17769 mg/L (60 min), 5-acetoacetamino benzimidazolone: 125.07 mg/L (60 min)).<sup>23</sup> The syntheses of the heterocycle-based azo compounds (Scheme 3, **24** and **25**) were fast (10 min) and quantitative.







**Scheme 3** Quantitative synthesis of azo compounds in the presence of granular PTFE in one pot<sup>a, b</sup>. <sup>a</sup>Reaction conditions: aniline (1.05 equiv), HCl (3.0 equiv), H<sub>2</sub>O (3 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g), mechanical stirring (400 rpm), rt, 20 min; coupling component (1 g). <sup>b</sup>All yields are quantitative. <sup>c</sup>Reaction conditions: H<sub>2</sub>SO<sub>4</sub> (10.0 equiv), NaNO<sub>2</sub> (1.10 equiv), and granular PTFE, rt, 5 min; 2,4-dinitroaniline or *o*-nitroaniline (1.05 equiv), 0 °C, 20 min; 2-naphthol (1 g), H<sub>2</sub>O (2 mL), rt, 60 min.

The recyclability of the reaction media was again explored using **10** (Scheme 3) as the test compound. As before, the mother liquid, granular PTFE and washing water from the filtration was used in the next cycle and an additional 1.0 equiv of HCl was added to each

cycle. This procedure was repeated 11 times. Each cycle took 60 min to reach completion and all the reactions were quantitative. At

the end of the 11th cycle, the volume of the mother liquor and washing water was 17 mL.

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**Table 5** Performance comparison between our method and the current industrial method for the synthesis of Pigment Red 3 (**10**) starting from 11 g of 2-naphthol

	Water consumed (mL)	HCl consumed (g)	NaOH consumed (g)	Surfactant consumed (g)	Yield (%)
This work	15	9.1	0	0	>99
Current industrial method <sup>8</sup>	450	27	10.5	0.22	93

We have repeated the reaction for preparing Pigment Red 3 (**10**) starting from 11 g of 2-naphthol according to the current industrial method.<sup>8</sup> A performance comparison between this method starting from 1 g of 2-naphthol in each of the 11 cycles and the current industrial method for the synthesis of Pigment Red 3 (**10**) is shown in Table 5. Obviously our method is superior to the current industrial method in all respects. The industrial method consumes much more water, HCl and NaOH; it requires the use of sulfonated castor oil (a surfactant); and the yield is lower.

With the exception of products **6**, **24** and **25**, all the other products (Table 2, **1-5** and Scheme 3, **7-23**) are organic industrial pigments. If our process could be adapted industrially, it should save large amounts of labor and energy and reduce or eliminate the use of water, bases, acids and surfactants. This would have tremendous positive environmental and economic impacts.

## Conclusions

In conclusion, one-step, one-pot and two-step, one-pot methods for the synthesis of azo pigments have been developed and applied to 22 industrial pigments. Compared to the current methods, these methods are fast, quantitative, pot-efficient and do not require the use of surfactants or bases to dissolve the coupling components. The granular PTFE, water and HCl used in the reaction are recyclable. These reactions can produce up to 22.7 g of product in the laboratory. If these methods are adapted for the industrial production of azo compounds, they will be cost efficient, environmentally friendly, save large amounts of labor, water and acids and eliminate the use of bases and surfactants. An *o*-nitro group effect, which is also applicable to classic synthesis, has been proposed to explain the differences in reaction rates.

## Experimental

**General information.** All of the chemicals were obtained from commercial sources. NMR spectra were recorded with a 400-MHz spectrometer for <sup>1</sup>H NMR and a 101-MHz instrument for <sup>13</sup>C NMR using TMS as an internal standard. Chemical shifts ( $\delta$ ) are reported relative to TMS (<sup>1</sup>H NMR), CDCl<sub>3</sub> or DMSO-d<sub>6</sub> (<sup>13</sup>C NMR). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Infrared analyses (KBr pellet) were performed by FTIR spectroscopy. High resolution mass spectroscopy (HRMS) using a quadrupole time of flight mass analyzer with electrospray ionization was used to analyze reaction products. All

aqueous reactions were conducted in 100-mL flasks (except for the 22.7-g-scale preparation which used 250-mL flasks). The reactions were agitated by a modified stirring rod.<sup>20,21,22</sup> The size of the granular PTFE was 30 pieces/g.

### General procedure for the preparations of azo pigments

For products **1-6**, a mixture of the coupling component (1 g), aromatic primary amine (1.05 equiv), HCl (2 equiv), H<sub>2</sub>O (3 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. Thin-layer chromatography (TLC) indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (2 mL) and dried to give a quantitative yield of the product without further purification.

For products **7-25**, a mixture of aromatic primary amine (1.05 equiv), HCl (3 equiv), H<sub>2</sub>O (3 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. After 20 min, the coupling component (1 g) was added. The reaction was continued until TLC indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (2 mL) and dried to give a quantitative yield of the product without further purification.

### Preparation of Pigment Red 4 (**7**) in 22.7 g scale

A mixture of 2-chloro-4-nitroaniline (1.05 equiv), HCl (3 equiv), H<sub>2</sub>O (45 mL), NaNO<sub>2</sub> (1.10 equiv, in 5 mL of H<sub>2</sub>O) and granular PTFE (12 g) was mechanically stirred (400 rpm) at rt. After 20 min, 2-naphthol (10 g) was added. The reaction was continued for 20 min and TLC was used to confirm the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (5 mL) and dried to give a quantitative yield of the product without further purification.

### Wastewater and excess HCl recycling in the preparation of Pigment Yellow 1 (**3**)

A mixture of acetoacetanilide (1 g), 4-methyl-2-nitroaniline (1.05 equiv), HCl (1.5 equiv), H<sub>2</sub>O (8 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. After 45 min, TLC indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were then filtered, washed with water (2 mL)



and dried to give a quantitative yield of the product without further purification. The remaining mother liquid and PTFE from the above reaction and the washing water from the filtration were combined and then used in place of the initial H<sub>2</sub>O in a second cycle. The amounts of acetoacetanilide, 4-methyl-2-nitroaniline, NaNO<sub>2</sub> and 2-naphthol were the same as for cycle 1 and the amount of added HCl was reduced to 1.1 equiv. In total, 11 cycles were conducted in this manner and all the reaction times from cycle 2 to cycle 11 were 30 min with quantitative yields. The combined volume of the mother liquid and washing water from the 11th cycle was 15.5 mL.

#### Wastewater and excess HCl recycling in the preparation of Pigment Red 3 (10)

A mixture of 4-methyl-2-nitroaniline (1.05 equiv), HCl (3 equiv), H<sub>2</sub>O (8 mL), NaNO<sub>2</sub> (1.10 equiv, in 2 mL of H<sub>2</sub>O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. After 20 min, 2-naphthol (1 g) was added. The reaction was continued for 60 min when TLC indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (2 mL) and dried to give a quantitative yield of the product without further purification. The granular PTFE, mother liquid and washing water from the filtration were then combined and used in a second cycle. The amounts of 4-methyl-2-nitroaniline, NaNO<sub>2</sub> and 2-naphthol were the same as for cycle 1 and the amount of added HCl was reduced to 1.0 equiv. Altogether 11 cycles were conducted in this same way. All the reactions were complete in 60 min and had quantitative yields. After the 11th cycle, the combined volume of the mother liquid and washing water was 17 mL.

#### Conflicts of interest

The authors declare no competing financial interest.

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