

Stable diazonium salts of weakly basic amines—Convenient reagents for synthesis of disperse azo dyes



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ABSTRACT

A new synthetic strategy for industrially important deep-shade disperse azo dyes was presented in this study. The key procedure is to prepare stable solid diazonium salts of weakly basic amines in the absence of concentrated sulfuric acid. Diazotization by *tert*-butyl nitrite in ethyl acetate was allowed to proceed in the presence of equivalent 1,5-naphthalenedisulfonic acid as stabilizer of diazonium salts and donor of hydrogen ion for the reaction. The separated solid diazonium salts exhibited good thermal stability. The corresponding disperse azo dyes were subsequently synthesized through the azo-coupling of the prepared solid diazonium salts with a range of aromatic tertiary amines. The azo dyes were produced in short reaction time, excellent yields, mild reaction conditions, simple experimental procedure and low energy consumption.

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1. Introduction

Azo dyes are compounds containing electron-donating (D) and electron-accepting (A) functional groups through an azo π -conjugated linker [1] and the D– π –A system has various electronic structures which can bring a full range of colors [2,3]. Hence, as industrially important chromophores, azo dyes are widely used in dyeing of natural and synthetic fibers [4,5], and many high technology fields, such as electronic devices, linear and nonlinear optics, reprography, sensors [6–8]. To date, approximately 3000 different azo dyes are used industrially which is the important guarantee for meeting people's demand for color [9,10].

Diazonium salts are precursors of the synthesis of azo dyes [11] and they are also widely used in organic synthesis such as Sandmeyer reaction [12], Balz–Schiemann reaction [13], carbon–carbon coupling reaction [14], and modification of polymeric materials and nanomaterials [15–17]. However, solid diazonium salts are very dangerous and have the tendency to explode because of their very poor thermal stability [18]. Thus, the diazotization of amines with sodium nitrite is usually carried out in the presence of excess hydrochloric or sulfuric acid solution and the obtained diazonium salt solution is directly poured into the coupling system to synthesize azo dyes resulting in large amounts of waste water containing

strong liquid acid. Considering the above constraints, strong solid acids as replacements for liquid acid catalysts [10,19], nitrite ionic liquid or nitrite-functionalized graphene quantum dots as effective nitrosonium sources [9,20] were reported to synthesize the corresponding azo dyes in excellent yields. Although each of these methods has specific merits, the substrates are simple aromatic amines or their derivatives, such as aniline, aminobenzenesulfonic acid and nitroaniline. Clean synthesis of azo dyes based on weakly basic amines is still a great challenge because they are very difficult to be diazotized due to their extremely weak alkalinity.

Weakly basic amines with two or three strong electron-withdrawing groups are the main raw materials on the preparation of dark disperse azo dyes with excellent color fastnesses [21]. However, their diazotization reactions using sodium nitrite are difficult to be carried out in hydrochloric or sulfuric acid solution because of their low reaction activity and solubility. In industrial production, the diazotization of weakly basic amines is always conducted in more than 10 times the molar quantity of concentrated sulfuric acid [22,23] and has to use nitrosyl sulfuric acid as nitrosating agent which has remarkable diazotization ability. Subsequently, the concentrated acid solution of diazonium salt is poured into the coupling system. Due to the strong dilution heat effect of concentrated sulfuric acid, large amounts of ice were used to maintain low temperature of the system to avoid the decomposition of the diazonium salt. Meanwhile, it is difficult to handle the high acid content waste water.

Herein, we present a practical preparation method of disperse

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azo dyes based on the novel stable solid diazonium salts of weakly basic amines. After the reactions of weakly basic amines with *tert*-butyl nitrite carried out in organic solution without any sulfuric acid in the presence of equivalent 1,5-naphthalenedisulfonic acid, the stable solid diazonium salts were obtained by simple filtration because of their very low solubility in organic solvent. The related disperse azo dyes were synthesized through the well-known azo-coupling reaction with aniline derivatives in good yields. Compared with traditional methods, coupling process can be conducted at room temperature, thus providing high reaction efficiency, excellent yields, mild reaction conditions, simple experimental procedure, and low energy consumption.

2. Experimental

2.1. General information

2,6-Dichloro-4-nitroaniline, 2-chloro-4-nitroaniline, 2,6-dibromo-4-nitroaniline, 2-amino-5-nitrobenzonitrile, 2,4-dinitroaniline, *N,N*-diethylaniline, *tert*-butyl nitrite and 1,5-naphthalenedisulfonic acid tetrahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,5-naphthalenedisulfonic acid tetrahydrate was dried at 130 °C under high vacuum (2.7 kPa) for 3 h. 3-(*N*-Ethylanilino)propionitrile, 3,3'-(phenylimino)dipropionitrile and *N*-[3-(diethylamino)phenyl]acetamide were purchased from Jiangsu Jihua Chemical Co., Ltd. The solvents were commercial analytical grade and used as received.

The diazotization was monitored by thin-layer chromatography on precoated silica gel glass based plates purchased from Branch of Qingdao Haiyang Chemical Co., Ltd and the yields of the diazonium salts were obtained by titration with the standard solution of *N,N*-diethylaniline at 0 °C–5 °C. The purity of dyes was determined by external standard method through an Agilent 1260 Infinity HPLC equipment. The diazonium salts and the dyes were all characterized by spectroscopic data with specified conditions. Tandem mass spectrometry (MS/MS) was recorded on a Thermo Scientific TSQ Quantum Ultra equipment with suitable collision energies. MS spectra and HRMS spectra were recorded on a Thermo Scientific LTQ Orbitrap XL mass spectrometer. FT-IR spectra were recorded as Nujol mulls or KBr disks using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. ¹H NMR spectra and ¹³C NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer using D₂SO₄ or DMSO-*d*₆ as the deuterated solvents. The absorption spectra were recorded on an Agilent HP 8453 UV–Vis spectrophotometer. Elemental analysis was performed on an Element Vario EL III Analyzer. Thermal decomposition temperature of the diazonium salts were obtained by thermogravimetric analysis (TGA) conducted on a NETZSCH TG 209 C TGA instrument at 5 °C/min from ambient temperature to 200 °C under air atmosphere.

2.2. Typical synthesis of stable solid diazonium salt of 2,4-dinitroaniline

2,4-Dinitroaniline (10 mmol) and 1,5-naphthalenedisulfonic acid (10 mmol) were dissolved in 100 mL ethyl acetate at 50 °C and the mixture was stirred for 10 min. *Tert*-butyl nitrite (15 mmol) was added by dropping to the mixture for about 2 min at 25 °C. The reaction solution was further stirred for 20 min with the temperature maintained at 25 °C. A salmon pink solid was obtained by suction filtration and air drying. The yield was 99.0%.

2.3. Characterization of the stable diazonium salts

2-Chloro-4-nitrobenzene diazonium salt (2a): MS/MS (10 eV), *m/z*: calcd for diazonium cation, 183.99; found, 184.03. ¹H NMR

(D₂SO₄) δ (ppm): 9.22 (2.00H, d, *J* = 8.7 Hz), 9.14–9.06 (3.72H, m), 8.94 (1.86H, dd, *J* = 9.1, 2.2 Hz), 8.85–8.76 (2.00H, m), 8.25 (2.00H, dd, *J* = 8.7, 7.5 Hz). FT-IR (Nujol mull, cm^{−1}): 3100, 3071, 2311, 2280, 1569, 1528, 1499, 1461, 1377, 1358, 1298, 1237, 1164, 1098, 1040. Anal. Calcd: C, 40.35; H, 1.88; N, 12.41%. Found: C, 39.63; H, 1.80; N, 12.54%.

2,6-Dibromo-4-nitrobenzene diazonium salt (2b): MS/MS (10 eV), *m/z*: calcd for diazonium cation, 307.85; found, 307.63. ¹H NMR (D₂SO₄) δ (ppm): 9.22 (2.00H, d, *J* = 8.8 Hz), 9.15 (1.82H, s), 8.79 (2.00H, dd, *J* = 7.4, 10 Hz), 8.23 (2.00H, dd, *J* = 8.8, 7.5 Hz). FT-IR (Nujol mull, cm^{−1}): 3084, 2288, 1561, 1539, 1499, 1460, 1377, 1345, 1292, 1231, 1199, 1176, 1152, 1076, 1043. Anal. Calcd: C, 32.29; H, 1.52; N, 7.06%. Found: C, 32.34; H, 1.44; N, 7.22%.

2,6-Dichloro-4-nitrobenzene diazonium salt (2c): MS/MS (5 eV), *m/z*: calcd for diazonium cation, 217.95; found, 218.18. ¹H NMR (D₂SO₄) δ (ppm): 9.21 (2.00H, d, *J* = 8.8 Hz), 8.98 (2.72H, s), 8.80 (2.00H, d, *J* = 7.5 Hz), 8.23 (2.00H, t, *J* = 8.2 Hz). FT-IR (Nujol mull, cm^{−1}): 3087, 2285, 1551, 1460, 1415, 1377, 1345, 1293, 1268, 1244, 1220, 1201, 1167, 1110, 1034, 1019. Anal. Calcd: C, 37.30; H, 1.61; N, 9.77%. Found: C, 36.33; H, 1.82; N, 9.11%.

2-Cyano-4-nitrobenzene diazonium salt (2d): MS/MS (8 eV), *m/z*: calcd for diazonium cation, 175.03; found, 175.28. ¹H NMR (D₂SO₄) δ (ppm): 9.65 (1.59H, d, *J* = 1.8 Hz), 9.48–9.41 (3.18H, m), 9.23 (2.00H, d, *J* = 8.8 Hz), 8.81 (2.00H, d, *J* = 7.5 Hz), 8.25 (2.00H, t, *J* = 8.2 Hz), 4.88 (1.58H, q, *J* = 7.1 Hz), 1.80 (1.05H, d, *J* = 14.2 Hz). FT-IR (Nujol mull, cm^{−1}): 3473, 3099, 2309, 2245, 1613, 1549, 1498, 1460, 1377, 1356, 1315, 1236, 1189, 1157, 1101, 1040. Anal. Calcd: C, 43.77; H, 2.23; N, 15.36%. Found: C, 43.04; H, 2.76; N, 14.79%.

2,4-Dinitrobenzene diazonium salt (2e): MS/MS (10 eV), *m/z*: calcd for diazonium cation, 195.01; found, 195.02. ¹H NMR (D₂SO₄) δ (ppm): 9.78 (1.85H, q, *J* = 2.0 Hz), 9.43 (3.70H, qd, *J* = 8.8, 5.0 Hz), 9.23 (2.00H, dd, *J* = 8.8, 2.9 Hz), 8.82 (2.00H, dd, *J* = 7.7, 2.9 Hz), 8.26 (2.00H, td, *J* = 8.3, 3.0 Hz). FT-IR (Nujol mull, cm^{−1}): 3099, 3076, 3043, 2312, 2287, 1612, 1591, 1546, 1498, 1462, 1377, 1348, 1331, 1246, 1227, 1215, 1201, 1163, 1142, 1111, 1090, 1036. Anal. Calcd: C, 39.11; H, 1.81; N, 16.00%. Found: C, 39.07; H, 1.82; N, 15.83%.

2.4. Typical procedure for coupling

N,N-Diethylaniline (10 mmol) was dissolved in 80 mL water with 1.2 mL 37% hydrochloric acid and then the salmon pink diazonium salt of 2,4-dinitroaniline was quickly added within 2 min at 0 °C–5 °C followed by adjusting the pH to 4–5 with 2 M NaOH solution. The reaction endpoint was confirmed by color reaction using H-acid. The precipitated dye was filtered, washed with water and dried at 80 °C to afford the crude product. The crude yield was 95.0% and the degree of purity was 97.0%.

2.5. Spectroscopic data of disperse azo dyes

Compound 4a: C₁₆H₁₇ClN₄O₂: MS, *m/z*: calcd for [M+H]⁺, 333.11; found, 333.10. HRMS, *m/z*: calcd for [M+H]⁺, 333.1113; found, 333.1115. ¹H NMR (DMSO-*d*₆) δ (ppm): 8.44 (1H, q, *J* = 2.5 Hz), 8.25 (1H, dq, *J* = 9.0, 2.5 Hz), 7.90–7.83 (2H, m), 7.83–7.76 (1H, m), 6.89 (2H, dt, *J* = 9.0, 2.8 Hz), 3.52 (4H, q, *J* = 7.2 Hz), 1.18 (6H, t, *J* = 6.9 Hz). ¹³C NMR (126 MHz, DMSO-*d*₆) δ (ppm): 152.49, 151.88, 146.59, 143.12, 132.11, 126.92, 125.67, 123.33, 117.95, 111.53, 44.38, 12.50. FT-IR (KBr, cm^{−1}): 3099, 2972, 2903, 1599, 1579, 1513, 1449, 1407, 1355, 1329, 1307, 1137, 1121, 1074, 1045, 1007, 887, 831, 819. UV (λ_{max} in acetone): 513 nm.

Compound 4b: C₁₆H₁₆Br₂N₄O₂: MS, *m/z*: calcd for [M+H]⁺, 456.97; found, 457.01. HRMS, *m/z*: calcd for [M+H]⁺, 456.9692; found, 456.9697. ¹H NMR (DMSO-*d*₆) δ (ppm): 8.56 (2H, s), 7.84–7.78 (2H, m), 6.90–6.83 (2H, m), 3.51 (4H, q, *J* = 7.1 Hz), 1.17 (6H, t, *J* = 7.0 Hz). ¹³C NMR (126 MHz, DMSO-*d*₆) δ (ppm): 155.23,

151.85, 145.67, 141.65, 127.78, 126.22, 115.16, 111.19, 44.32, 12.44. FT-IR (KBr, cm^{-1}): 3084, 2971, 1601, 1521, 1394, 1355, 1336, 1273, 1253, 1191, 1163, 1131, 1072, 1051, 1007, 888, 819. UV (λ_{max} in acetone): 441 nm.

Compound 4c: $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{N}_4\text{O}_2$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 367.07; found, 367.08. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 367.0723; found, 367.0724. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.43 (2H, s), 7.84–7.78 (2H, m), 6.90–6.83 (2H, m), 3.51 (4H, q, $J = 7.0$ Hz), 1.17 (6H, t, $J = 7.0$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 153.12, 151.93, 145.21, 142.09, 126.77, 126.28, 124.46, 111.20, 44.33, 12.43. FT-IR (KBr, cm^{-1}): 3089, 2974, 1603, 1521, 1396, 1355, 1340, 1274, 1253, 1192, 1148, 1127, 1061, 1008, 887, 821. UV (λ_{max} in acetone): 443 nm.

Compound 4d: $\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 324.15; found, 324.13. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 324.1455; found, 324.1457. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.83 (1H, s), 8.52 (1H, dd, $J = 9.1$, 2.6 Hz), 7.95 (1H, d, $J = 9.1$ Hz), 7.89 (2H, d, $J = 8.9$ Hz), 7.01–6.90 (2H, m), 3.56 (4H, q, $J = 7.0$ Hz), 1.19 (6H, t, $J = 7.1$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 157.22, 152.71, 145.79, 142.96, 129.50, 128.92, 127.54, 117.43, 115.62, 111.96, 110.29, 44.58, 12.53. FT-IR (KBr, cm^{-1}): 3077, 2975, 2931, 2229, 1597, 1577, 1516, 1414, 1355, 1324, 1271, 1249, 1171, 1136, 1117, 1071, 1007, 907, 838, 823. UV (λ_{max} in acetone): 536 nm.

Compound 4e: $\text{C}_{16}\text{H}_{17}\text{N}_5\text{O}_4$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 344.14; found, 344.14. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 344.1353; found, 344.1354. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.89–8.83 (1H, m), 8.50 (1H, ddd, $J = 9.2$, 6.5, 2.6 Hz), 7.95–7.87 (1H, m), 7.77 (2H, ddd, $J = 9.6$, 5.0, 2.1 Hz), 6.90 (2H, td, $J = 7.1$, 5.4, 2.1 Hz), 3.58–3.49 (4H, m), 1.21–1.14 (6H, m). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 152.48, 148.07, 145.99, 145.39, 143.00, 127.55, 127.37, 119.80, 119.18, 111.77, 44.52, 12.48. FT-IR (KBr, cm^{-1}): 3100, 2976, 2931, 1592, 1516, 1411, 1353, 1328, 1271, 1196, 1134, 1113, 1066, 911, 831, 822. UV (λ_{max} in acetone): 529 nm.

Compound 4f: $\text{C}_{17}\text{H}_{15}\text{Br}_2\text{N}_5\text{O}_2$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 481.96; found, 482.12. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 481.9645; found, 481.9649. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.82–8.33 (2H, m), 7.88–7.79 (2H, m), 7.01–6.94 (2H, m), 3.80 (2H, t, $J = 6.8$ Hz), 3.57 (2H, q, $J = 7.0$ Hz), 2.85 (2H, t, $J = 6.8$ Hz), 1.18 (3H, t, $J = 7.0$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 155.12, 151.51, 145.82, 142.35, 127.77, 125.94, 119.15, 115.01, 111.80, 45.41, 44.66, 15.72, 12.04. FT-IR (KBr, cm^{-1}): 3100, 3066, 2970, 2933, 2248, 1600, 1522, 1399, 1342, 1280, 1245, 1142, 1077, 1054, 881, 825. UV (λ_{max} in acetone): 421 nm.

Compound 4g: $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{N}_5\text{O}_2$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 392.07; found, 392.20. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 392.0676; found, 392.0677. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.42 (2H, s), 7.83 (2H, d, $J = 9.0$ Hz), 6.97 (2H, d, $J = 9.1$ Hz), 3.81 (2H, t, $J = 6.8$ Hz), 3.58 (2H, q, $J = 7.0$ Hz), 2.85 (2H, t, $J = 6.7$ Hz), 1.18 (3H, t, $J = 7.0$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 152.99, 151.59, 145.40, 142.76, 126.66, 125.99, 124.46, 119.12, 111.80, 45.41, 44.67, 15.70, 12.03. FT-IR (KBr, cm^{-1}): 3059, 2980, 2252, 1604, 1572, 1529, 1519, 1394, 1336, 1311, 1280, 1148, 1134, 1078, 1065, 884, 822. UV (λ_{max} in acetone): 423 nm.

Compound 4h: $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}_2$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 349.14; found, 349.25. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 349.1408; found, 349.1412. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.84 (1H, d, $J = 2.6$ Hz), 8.54 (1H, dd, $J = 9.1$, 2.6 Hz), 7.96 (1H, d, $J = 9.1$ Hz), 7.90 (2H, d, $J = 8.9$ Hz), 7.04 (2H, d, $J = 9.3$ Hz), 3.84 (2H, t, $J = 6.8$ Hz), 3.61 (2H, $J = 7.1$ Hz), 2.87 (2H, t, $J = 6.7$ Hz), 1.24–1.15 (m, 3H). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 156.82, 152.29, 146.18, 143.47, 129.41, 128.92, 127.09, 119.01, 117.54, 115.44, 112.32, 110.76, 45.48, 44.86, 15.74, 12.15. FT-IR (KBr, cm^{-1}): 3080, 2919, 2248, 2231, 1600, 1595, 1577, 1525, 1518, 1411, 1340, 1325, 1309, 1290, 1173, 1133, 1121, 910, 842, 825. UV (λ_{max} in acetone): 511 nm.

Compound 4i: $\text{C}_{18}\text{H}_{15}\text{ClN}_6\text{O}_2$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 383.10; found, 383.15. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 383.1018; found,

383.1021. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.45 (1H, ddd, $J = 7.4$, 4.6, 2.4 Hz), 8.26 (1H, ddt, $J = 8.9$, 6.0, 2.2 Hz), 7.88 (2H, ddd, $J = 9.4$, 4.5, 2.3 Hz), 7.81–7.73 (1H, m), 7.09 (2H, dt, $J = 9.4$, 2.2 Hz), 3.89 (4H, t, $J = 7.0$ Hz), 2.86 (4H, t, $J = 6.9$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 152.11, 150.78, 147.27, 144.25, 132.64, 126.29, 125.73, 123.37, 118.99, 118.24, 112.55, 45.68, 15.40. FT-IR (KBr, cm^{-1}): 2958, 2250, 1600, 1514, 1404, 1362, 1339, 1314, 1151, 1121, 1046, 888, 832. UV (λ_{max} in acetone): 459 nm.

Compound 4j: $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{N}_6\text{O}_2$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 417.06; found, 417.06. HRMS, m/z : calcd for $[\text{M}+\text{Na}]^+$, 339.0448; found, 439.0447. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.43 (2H, dd, $J = 6.4$, 1.9 Hz), 7.85 (2H, d, $J = 9.2$ Hz), 7.09 (2H, d, $J = 9.2$ Hz), 3.89 (4H, t, $J = 6.8$ Hz), 2.86 (4H, t, $J = 6.8$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 152.88, 150.97, 145.59, 143.38, 126.55, 125.78, 124.49, 119.00, 112.38, 45.66, 15.36. FT-IR (KBr, cm^{-1}): 3079, 2918, 2247, 1603, 1568, 1518, 1406, 1377, 1345, 1249, 1208, 1147, 1062, 1026, 900, 831. UV (λ_{max} in acetone): 405 nm.

Compound 4k: $\text{C}_{18}\text{H}_{19}\text{Br}_2\text{N}_5\text{O}_3$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 513.99; found, 513.99. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 513.9907; found, 513.9913. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 10.23 (1H, s), 8.54 (2H, s), 7.93 (1H, d, $J = 3.0$ Hz), 7.72 (1H, d, $J = 9.4$ Hz), 6.67 (1H, dd, $J = 9.5$, 2.8 Hz), 3.51 (4H, q, $J = 7.1$ Hz), 2.15 (3H, s), 1.20 (6H, t, $J = 7.0$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 169.25, 153.78, 153.28, 145.15, 139.97, 130.28, 128.06, 123.12, 116.07, 107.94, 100.07, 44.76, 25.06, 12.51. FT-IR (KBr, cm^{-1}): 3091, 2981, 2930, 1690, 1622, 1616, 1529, 1513, 1494, 1336, 1291, 1184, 1167, 1125, 1074, 1055, 1005, 890, 873, 858. UV (λ_{max} in acetone): 491 nm.

Compound 4l: $\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{N}_5\text{O}_3$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 424.09; found, 424.23. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 424.0938; found, 424.0950. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 10.30 (1H, s), 8.41 (2H, d, $J = 1.0$ Hz), 7.91 (1H, d, $J = 2.7$ Hz), 7.71 (1H, d, $J = 9.5$ Hz), 6.67 (1H, dd, $J = 9.4$, 2.7 Hz), 3.51 (4H, q, $J = 7.1$ Hz), 2.14 (3H, s), 1.20 (6H, t, $J = 7.0$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 169.26, 153.34, 151.91, 144.66, 139.95, 130.92, 127.42, 124.66, 123.25, 108.00, 100.16, 44.78, 24.94, 12.51. FT-IR (KBr, cm^{-1}): 3353, 3103, 2980, 2935, 2901, 1704, 1607, 1552, 1531, 1495, 1419, 1350, 1330, 1256, 1172, 1111, 1064, 1005, 901, 886, 855. UV (λ_{max} in acetone): 496 nm.

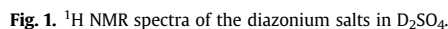
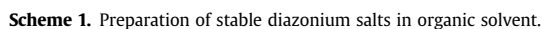
Compound 4m: $\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_5$: MS, m/z : calcd for $[\text{M}+\text{H}]^+$, 401.16; found, 401.22. HRMS, m/z : calcd for $[\text{M}+\text{H}]^+$, 401.1568; found, 401.1573. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 10.69 (1H, s), 8.83 (1H, d, $J = 2.5$ Hz), 8.47 (1H, dd, $J = 9.1$, 2.5 Hz), 8.18 (1H, d, $J = 9.1$ Hz), 7.95 (1H, d, $J = 2.7$ Hz), 7.75–7.63 (1H, m), 6.73 (1H, dd, $J = 9.5$, 2.8 Hz), 3.53 (4H, q, $J = 7.1$ Hz), 2.21 (3H, s), 1.20 (6H, t, $J = 7.0$ Hz). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ (ppm): 169.70, 153.93, 148.27, 145.13, 144.54, 132.33, 127.39, 123.76, 119.95, 119.40, 109.02, 100.47, 9.48, 45.02, 24.88, 12.58. FT-IR (KBr, cm^{-1}): 3448, 3095, 2975, 2935, 1693, 1624, 1593, 1567, 1520, 1488, 1419, 1323, 1279, 1254, 1193, 1172, 1137, 1117, 1078, 897, 858, 845, 831. UV (λ_{max} in acetone): 546 nm.

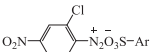
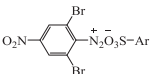
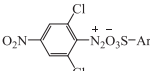
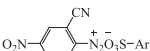
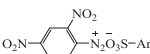
3. Results and discussion

3.1. Preparation and characterization of stable solid diazonium salts

The solid diazonium salts of aromatic amines were conveniently obtained by simple filtration after the reactions of weakly basic amines with *tert*-butyl nitrite which were carried out in organic solution in the presence of equivalent 1,5-naphthalenedisulfonic acid (Scheme 1). The structures of diazonium salts were confirmed by FT-IR and tandem mass spectrometry according to references [24,25].

Optimization of the diazotization conditions was investigated with different molar ratios of the aromatic amine, 1,5-naphthalenedisulfonic acid and *tert*-butyl nitrite and the optimal ratio was 1:1:1.5. The new diazonium salts of weakly basic amines



Entry	Amine	Diazonium salt	Structure number	Ratio of structures A and B
1	1a		2a	0.14:0.86
2	1b		2b	1.00:0.00
3	1c		2c	0.64:0.36
4	1d		2d	0.41:0.59
5	1e		2e	0.15:0.85

Reaction temperatures were stipulated in accordance with different substrates (Table 2). Although diazotization proceeded without any concentrated sulfuric acid or nitrosyl sulfuric acid, the reaction efficiency was very high. As a result, the very low basic amine, 2,4-dinitroaniline, could be diazotized completely within a short time (22 min, Table 2, entry 5). The diazotization times of three substrates (Table 2, entries 3–5) were much less than that of the traditional methods [28–30]. Meanwhile, the yields of the diazonium salts were excellent (Table 2). The high reaction efficiency may be attributed to the formation of nitrosonium cation

Entry	Structure number	Temperature (°C)	Reaction time (min)		Yield (%)	Thermal decomposition temperature (°C)
			Found	Reported [Ref.]		
1	2a ^a	0	60	60 [26]	92.8	164.4
2	2b	50	120	120 [27]	93.1	175.5
3	2c	22	17	120 [28]	98.0	125.7
4	2d	0	60	120 [29]	89.7	115.9 ^b
5	2e	25	22	120 [30]	99.0	121.9

^b There was a continuous lower decline of the TG curves before 115.9 °C.

(⁺NO) [31] in the presence of 1,5-naphthalenedisulfonic acid and *tert*-butyl nitrite.

3.2. Thermal stability of solid diazonium salts

TGA was used to characterize the thermal stability of the diazonium salts. The initial thermal decomposition temperatures of 2a, 2b, 2c, 2d, and 2e are 164.4, 175.5, 125.7, 115.9, and 121.9 °C, respectively (Table 2 and Fig. 2). Thus, the prepared diazonium salts of weakly basic amines are thermostable and can be stored at room temperature in dried state without disintegration.

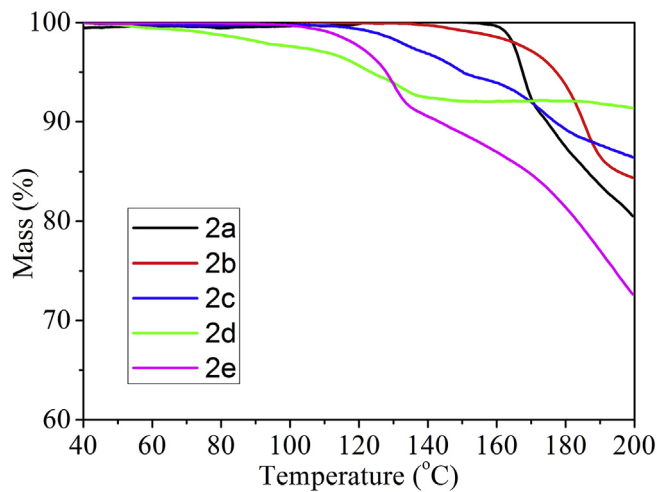


Fig. 2. Thermogravimetric curves of five stable solid diazonium salts.

3.3. Synthesis of disperse azo dyes

The disperse azo dyes were synthesized by the well-known azo-coupling reaction between the as-prepared stable diazonium salts and the tertiary anilines at 0 °C–5 °C (Scheme 2). The pH of the coupling system was adjusted and maintained at 4–6 by 2 M NaOH

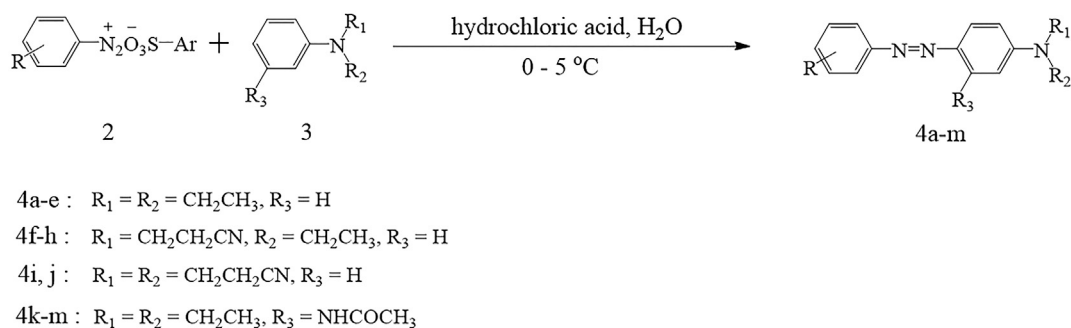
solution. The crude yields and purities of the relevant disperse azo dyes are shown in Table 3.

The coupling time of the present method was all much shorter than those reported in the literature (a few to dozens of minutes, Table 3, entries 1, 6, and 9). The reaction ability of the tertiary anilines is restricted by concentrated sulfuric acid in traditional methods. However, large amounts of concentrated acid were replaced in the present method by equivalent organic acid in contrast to amines during diazotization. Consequently, the coupling reaction could be conducted with short time at low concentration acid.

Compared with traditional coupling technology, the present method does not employ the dilution process of concentrated sulfuric acid because of the usage of solid diazonium salts. Thus, the generation of a large amount of heat produced from the dilution of sulfuric acid in the traditional coupling process was avoided. Meanwhile, the thermal analysis results of solid diazonium salts show that their thermal stabilities are sufficient. Therefore, it is not needed to use a lot of ice to keep the system at low temperature or even the reaction can be carried out at normal temperature without any cooling process. Compounds 4a, 4c, and 4d were chosen as objects of study and prepared with different temperatures. The yields of the dyes are shown in Fig. 3, which indicate no significant reducing of the yield during temperature increase. These results show that this new technology is of great significance for the realization of energy saving and emission reduction in the production of disperse azo dyes based on weakly basic amines.

4. Conclusion

A novel strategy for synthesis of industrial disperse azo dyes based on weakly basic amines is presented. The key advantage of this new procedure is the formation and simple separation of stable solid diazonium salts of weakly basic amines. This new procedure can avoid the strong heat effect coming from the dilution of concentrated sulfuric acid in the traditional coupling process. Large amounts of ice were saved and the generation of highly concentrated acidic waste water was prevented. For these reasons, the efficient, rapid and economical synthesis of disperse azo dyes employing stable solid diazonium salts has a very good prospect in the industrial application.



Scheme 2. Azo-coupling of stable diazonium salts with tertiary aniline derivatives.

Table 3
Synthesis of azo dyes using stable diazonium salts.

Entry	Diazonium salt	Coupling reagent	Product	Structure number	Reaction time (min)		Crude yield (%) ^a	Purity (%)
					Found	Reported [Ref.]		
1	2a			4a	5	120 [32]	92.6	95.9
2	2b			4b	5	—	90.8	97.9
3	2c			4c	5	—	88.5	97.7
4	2d			4d	5	—	90.9	88.8
5	2e			4e	5	—	95.0	97.0
6	2b			4f	12	120 [27]	93.5	96.7
7	2c			4g	10	—	96.1	96.0
8	2d			4h	16	—	94.7	87.3
9	2a			4i	40	300 [26]	94.8	96.6
10	2c			4j	19	—	94.0	90.9
11	2b			4k	6	—	94.3	91.6
12	2c			4l	19	—	95.9	91.5
13	2e			4m	34	—	95.9	89.3

^a The crude yields of disperse azo dyes were calculated based on the initial weakly basic amines.

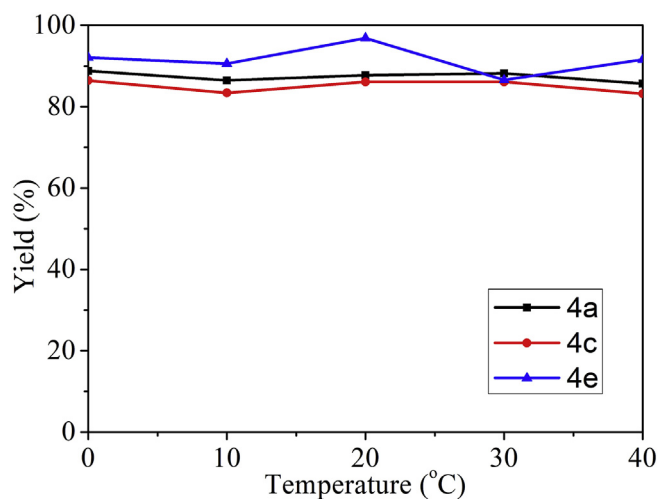


Fig. 3. Yields of three representative dyes at different coupling temperatures (Yield = Crude yield × Purity).

Acknowledgments

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