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Parallel Synthesis of Strongly Fluorescent Polysubstituted 2,6-Dicyanoanilines via Microwave-Promoted Multicomponent Reaction

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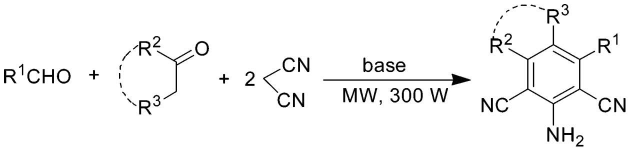
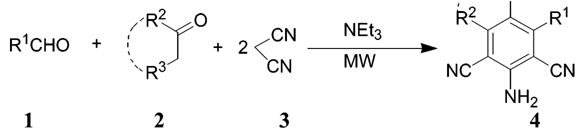


A facile parallel synthesis of polysubstituted 2,6-dicyanoanilines via microwave-promoted three-component reaction of aldehydes, ketones, and propanedinitrile in solution and also on polymer support has been developed. The screening for optical properties identified two new compounds with high fluorescence quantum yields.

Coupled with the concomitant emergency of high-throughput screening, combinatorial chemistry techniques have evolved very rapidly over the past years and are playing significant roles in the development of modern synthetic organic chemistry.[1] To date, the concepts of combinatorial chemistry have been successfully applied to development and improvement of novel pharmaceutics, materials [1e] and catalysts using rapid parallel and mix-and-split synthesis in solution and also on polymer supports. Lately, multicomponent reactions (MCRs) involving domino process with at least three different simple substrates has emerged as a powerful strategy.[2] This methodology allows molecular complexity and diversity to be created by the facile formation of several new covalent bonds in a one-pot transformation quite closely approaching the concept of an ideal synthesis and is particularly well adapted for combinatorial synthesis.[3]

In the past decades, photoinduced intramolecular electron transfer has been a subject of extensive study. The molecule in which electron transfer can be approached comprises a single donor and a single acceptor. To obtain a long-lived charge separation, much attention has been devoted to the investigation of the acceptor−donor-acceptor (A−D−A) systems comprising one electron donor and two electron acceptors.[4] This considerable research effort is justified by the potential applications of these molecular systems, which are the basis for artificial photosynthetic systems,[5] materials presenting semiconducting or nonlinear optical properties,[6] and molecular electronic devices.[7]

SCHEME 1. MW-Promoted Efficient Synthesis of Polysubstituted 2,6-Dicyanoanilines



2,6-Dicyanoanilines are typical A−D−A systems. However, the investigation of the optical properties of this system has rarely been documented.[8] 2,6-Dicyanoanilines were reported to be prepared from arylidenemalonodinitriles and 1-arylethylidenemalonodinitriles in the presence of piperidine.[8a] The reaction between propanedinitrile and α,β-unsaturated ketones could also give 2,6-dicyanoanilines, but the yields were very poor ($5\sim20\%$).[9] To improve the utility of this process, we developed its practical multicomponent variant described herein. The α,β-unsaturated ketones are generated in situ from the corresponding aldehydes and ketones, whereupon they are captured by 2 equivalents of propanedinitrile, forming the corresponding polysubstituted 2,6-dicyanoanilines (Scheme 1). Performing both steps of this process under microwave irradiation significantly reduces the reaction time and increases the yields. As the starting point of our exploration, we chose the reaction between aldehyde **1a** and ketone **2c**. A mixture of aldehyde, ketone and propanedinitrile (2.5 equiv) was irradiated in the presence of a base, such as triethylamine or piperidine, for 2 min to give substituted 2,6-dicyanoaniline. The best

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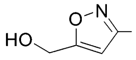
TABLE 1. Parallel Solution-Phase Synthesis of Polysubstituted 2,6-Dicyanoanilines

Entry	R^1	R^2	R^3	Product	Isolated Yield (%)
1	C_6H_5 (**1a**)	C_6H_5 (**2a**)	Me (**2a**)	**4a**	55
2	4-MeC_6H_4 (**1b**)	**2a**	**2a**	**4b**	52
3	4-$MeO_2CC_6H_4$ (**1c**)	**2a**	**2a**	**4c**	56
4	4-FC_6H_4 (**1d**)	**2a**	**2a**	**4d**	58
5	4-ClC_6H_4 (**1e**)	**2a**	**2a**	**4e**	53
6	2-ClC_6H_4 (**1f**)	**2a**	**2a**	**4f**	55
7	2,6-$Cl_2C_6H_3$ (**1g**)	**2a**	**2a**	**4g**	59
8	Furan-2-yl (**1h**)	**2a**	**2a**	**4h**	60
9	**1b**	4-MeC_6H_4 (**2b**)	Me (**2b**)	**4i**	55
10	3,4,5-$(MeO)_3C_6H_2$ (**1i**)	**2b**	**2b**	**4j**	50
11	**1f**	**2b**	**2b**	**4k**	56
12	**1g**	**2b**	**2b**	**4l**	58
13	**1a**	Me (**2c**)	H (**2c**)	**4m**	56
14	**1h**	**2c**	**2c**	**4n**	51
15	**1f**	Et (**2d**)	Me (**2d**)	**4o**	55
16	**1b**	$(CH_2)_3$ (**2e**)		**4p**	53
17	**1a**	$(CH_2)_4$ (**2f**)		**4q**	54
18	3,4-$(OCH_2O)C_6H_3$ (**1j**)	**2f**		**4r**	57
19	**1f**	**2f**		**4s**	57
20	**1f**	2-$C_6H_4CH_2CH_2$ (**2g**)		**4t**	63
21	**1a**	 (**2h**)	H (**2h**)	**4u**	61

conditions were found to be 300 W irradiation power. The product, 3-methyl-5-phenyl-2,6-dicyanoaniline (**4m**), has been isolated in 56% yield (Table 1, entry 13). This prompted us to extend our studies toward the incorporation of different aldehydes and ketones.

Using this three-component one-pot procedure, we synthesized a parallel library containing 21 polysubstituted 2,6-dicyanoanilines (Table 1). The yields (50−63%) are extensively increased as compared with the published methods (5−20%).[9] The crystallographic structure of compound **4c** was determined by X-ray diffraction (see the Supporting Information), which is in accordance with the ^{1}H NMR, ^{13}C NMR, and HRMS spectra.

In connection with our research on the liquid-phase synthesis,[10] we also synthesized the 2,6-dicyanoanilines using poly(ethylene glycol) (PEG) as support (Scheme 2). The PEG-bound aldehydes **5**[10a] were mixed with ketones **2** and 3 equivalents of propanedinitrile (**3**). NH_4OAc was used as the base. The one-pot three-component reaction was carried out under the microwave irradiation for 2 min. The resulting PEG bound 2,6-dicyanoanilines **6** were cleaved by NaOMe/MeOH to afford free polysubstituted 2,6-dicyanoanilines **7**. As exemplified in Table 2, the reactions proceeded smoothly to completion, and the products were isolated in good yields (65−82%) and high purities (89−98%).

It is interesting for us to screen the polysubstituted 2,6-dicyanoanilines for their optical properties. The correlation between optical properties (especially emission wavelengths and the fluorescence quantum yields) and the molecular structures can currently be described only empirically, since no detailed theoretical predictions are possible.[11] A large number of compounds in a combinatorial library should correlate to a better understanding of the inherent structure−property relationships from which specifically tailored materials can be produced. From the library, two members **4p** and **4u** with the most intensive fluorescence were selected. Maximum emission wavelengths (λ_{em} = 395−440 nm) were observed for these two compounds in CH_2Cl_2, MeOH, and THF, while the corresponding fluorescent quantum yields (Φ_f = 0.08−

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SCHEME 2. MW-Promoted Liquid-Phase Synthesis of Polysubstituted 2,6-Dicyanoanilines

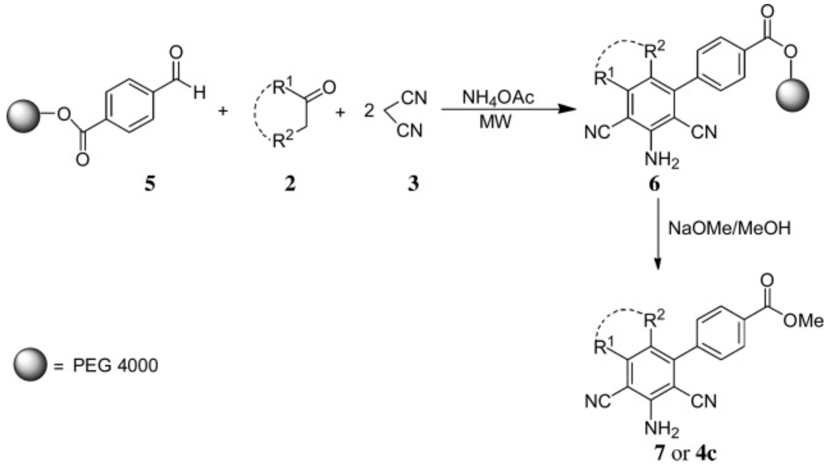

TABLE 2. MW-Promoted Parallel Liquid-Phase Synthesis of 2,6-Dicyanoanilines Using PEG as Support

entry	R^1	R^2	product	isolated yield(%)	purity[a] (%)
1	C_6H_5 (**2i**)	H (**2i**)	**7a**	80	93
2	C_6H_5 (**2a**)	Me (**2a**)	**4c**	82	93
3	4-MeC_6H_4 (**2b**)	Me (**2b**)	**7c**	81	96
4	Me (**2c**)	H (**2c**)	**7d**	65	95
5	4-FC_6H_4 (**2j**)	H (**2j**)	**7e**	77	95
6	$(CH_2)_3$ (**2e**)		**7f**	79	96
7	$(CH_2)_4$ (**2f**)		**7g**	78	98
8	Et (**2d**)	Me (**2d**)	**7h**	73	89
9	2-$C_6H_4CH_2CH_2$ (**2g**)		**7i**	75	90

[a] Purity data were obtained on the basis of HPLC analysis for the crude products.

TABLE 3. Fluorescence Data for Compounds 4p and 4u in Different Solvents

	in CH_2Cl_2			in MeOH			in THF		
compd	λ_{ex} (nm)	λ_{em} (nm)	Φ_f	λ_{ex} (nm)	λ_{em} (nm)	Φ_f	λ_{ex} (nm)	λ_{em} (nm)	Φ_f
4p	356	395	0.10	362	415	0.13	363	409	0.12
4u	368	414	0.08	373	433	0.10	374	440	0.09

0.13) were calculated based on 9,10-diphenylanthrance (Table 3).[12] In view of possible applications of these compounds (e.g., as organic light-emitting diodes) the NH_2 substituted A–D–A systems are of interest since these compounds can be transformed into more thermostable derivatives through their amino groups. Also, the subsequent step of the combinatorial development process, namely structural optimization should be possible. The application of combinatorial strategies for screening and optimization of organic charge-transporting materials in a spatially addressable library of organic light-emitting diodes was reported by Schmidt et al.[13]

In conclusion, we have demonstrated a facile and general microwave-enhanced three-component reaction for generation of polysubstituted 2,6-dicyanoaninilines. Using this one-pot protocol, the parallel synthesis of a large number of unpublished fluorescent 2,6-dicyanoaninilines in solution and also on soluble polymer support was achieved. Furthermore, two compounds with high fluorescent quantum yields were identified by screening the library for optical properties.

Experimental Section

General Procedure for Microwave-Promoted Parallel Synthesis of 2,6-Dicyanoanilines in solution. The appropriate (see Table 1) aldehydes (10 mmmol), ketones (10 mmol), propanedinitrile (25 mmol), and triethylamine (15 mmol) were placed in five individual 25 mL glass bottles immersed in a Pyrex crystallization dish filled with neutral alumina (500 g, 100–200 mesh). This setup was placed at the cavity of microwave synthesizer. After irradiation at 300 W for 2 min, the reaction mixture was cooled to room temperature and then dissolved in CH_2Cl_2. The solution was washed with water, dried over anhydrous Na_2SO_4 and evaporated in a vacuum. The crude products were purified by a flash column chromatography on silica gel with ethyl acetate–hexane (1:4, v/v) as eluent. All the compounds were recrystallized from ethanol.

2,6-Dicyano-3-(4-methyloxycarbonylphenyl)-4-methyl-5-phenylaniline (4c): colorless crystal needle; mp 210–213 °C; ^{1}H NMR ($CDCl_3$) δ 8.18 (d, J = 8.20 Hz, 2H), 7.48 (m, 3H), 7.39 (d, J = 8.20 Hz, 2H), 7.27 (t, J = 7.84 Hz, 2H), 5.16 (bs, 2H), 3.95 (s, 3H), 1.73 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$) δ 166.6, 151.1, 150.0, 149.6, 142.4, 137.6, 131.0, 130.4, 129.3, 129.1, 128.9, 128.6, 124.9, 115.6, 115.5, 98.7, 97.7, 52.6, 17.8 ppm; IR (KBr) ν 3457, 3345, 3245, 2950, 2223, 1718, 1644, 1560, 1436, 1278, 1116, 760, 702 cm^{-1}; MS (ESI) m/z 366.2 ([M − H]$^+$); HRMS (ESI) calcd for $C_{23}H_{17}N_3O_2$ ([M + Na]$^+$) 390.1213, found 390.1206.

2,6-Dicyano-3-(furan-2-yl)-4-methyl-5-phenylaniline (4h): olivine crystal needle; mp 198–199 °C; ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 0.94 Hz, 1H), 7.50 (m, 3H), 7.27 (m, 2H), 6.80 (d, J = 3.25 Hz, 1H), 6.59 (m, 1H), 5.18 (bs, 2H), 1.96 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$) δ 151.2, 150.4, 148.9, 144.1, 138.5, 137.7, 129.3, 129.1, 128.7, 125.9, 116.1, 115.7, 113.8, 111.8, 98.6, 96.6, 18.2 ppm; IR (KBr) ν 3459, 3359, 3242, 2930, 2221, 1639, 1555, 1454, 1268, 1026, 770, 714, 594 cm^{-1}; MS (ESI) m/z 298.1 ([M − H]$^+$); HRMS (ESI) calcd for $C_{19}H_{13}N_3O$ ([M + Na]$^+$) 322.0951, found 322.0960.

2,6-Dicyano-3,5-di(4-methylphenyl)-4-methylaniline (4i): white crystal needle; mp 251–253 °C; ^{1}H NMR ($CDCl_3$) δ 7.29 (d, J = 8 Hz, 4H), 7.18 (d, J = 8 Hz, 4H), 5.11 (bs, 2H), 2.41 (s, 6H), 1.76 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$) δ 150.9, 150.0, 139.0, 135.0, 130.0, 128.5, 125.3, 116.0, 98.0, 21.6, 17.9 ppm; IR (KBr) ν 3464, 3353, 3325, 2923, 2224, 1634, 1556, 1515, 1438,

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(12) Optically dilute measurements with refractive-index corrections, maximal absorption of solutions ≤0.04. Measurements referenced to 9,10-diphenylanthrance (Φ_f = 0.90 ± 0.02); (a) Lakowicz, J. R., Ed.; *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999. (b) Demas, J. N.; Grosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024.

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1265, 1020, 815, 528 cm^{-1}; MS (ESI) *m/z* 336.2 ([M − H]$^+$); HRMS (ESI) calcd for $C_{23}H_{19}N_3$ ([M + Na]$^+$) 360.1471, found 360.1473.

2,6-Dicyano-3-(2-chlorophenyl)-4-methyl-5-ethylaniline (4o): white crystal; mp 193−194 °C; ^{1}H NMR (CDCl$_3$) δ 7.53 (m, 1H), 7.41 (m, 2H), 7.20 (m, 1H), 5.07 (bs, 2H), 2.91 (q, J = 7.54 Hz, 2H), 1.92 (s, 3H), 1.27 (t, J = 7.55 Hz, 3H) ppm; ^{13}C NMR (CDCl$_3$) δ 152.8, 150.2, 147.7, 136.9, 132.9, 130.6, 130.2, 130.2, 127.6, 125.3, 115.8, 115.4, 98.0, 96.6, 27.0, 15.3, 14.0 ppm; IR (KBr) ν 3472, 3346, 3241, 2970, 2228, 2212, 1641, 1569, 1461, 1294, 1238, 1061, 895, 766, 540 cm^{-1}; MS (ESI) *m/z* 294.0 ([M − H]$^+$); HRMS (ESI) calcd for $C_{17}H_{14}ClN_3$ ([M + Na]$^+$) 318.0768, found 318.0763.

2,6-Dicyano-5-(5-hydroxylmethyl)isoxazol-3-yl)-3-phenylaniline (4u): yellowish solid; mp 226−228 °C; ^{1}H NMR (DMSO-d_6) δ 7.64 (m, 2H), 7.55 (m, 3H), 7.10 (s, 1H), 7.01 (s, 1H), 6.95 (bs, 2H), 5.79 (t, J = 5.79 Hz, 1H), 4.67 (d, J = 5.95 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6) δ 174.8, 160.1, 154.7, 150.9, 137.5, 136.6, 130.1, 129.2, 129.0, 118.1, 116.1, 115.1, 102.3, 96.8, 93.4, 55.2 ppm; IR (KBr) ν 3469, 3414, 3343, 3245, 2932, 2227, 2212, 1644, 1585, 1435, 1291, 1040, 704, 594 cm^{-1}; MS (ESI) *m/z* 315.0 ([M − H]$^+$); HRMS (EI) calcd for $C_{18}H_{12}N_4O_2$ (M$^+$) 316.0954, found 316.0951.

General Procedure for Microwave-Promoted Parallel Synthesis of 2,6-Dicyanoanilines on PEG Support. The appropriate (see Table 2) PEG-supported aldehydes (10 mmmol), ketones (20 mmol), propanedinitrile (30 mmol), and ammonium acetate (10 mmol) were placed in five individual 25 mL glass bottles immersed in a Pyrex crystallization dish. This setup was placed at the cavity of microwave synthesizer. After irradiation at 300 W for 2 min, the reaction mixtures were cooled to room temperature. The polymer-supported products **6** were crystallized from 2-propanol (30 mL), washed with diethyl ether, and subsequently dried in a vacuum. The polymers **6** were treated with 0.1 N NaOMe in anhydrous MeOH (10 mL) at room temperature for 6 h. The detached PEG-OH was precipitated by adding cold diethyl ether (30 mL) and filtered. The filtrates were washed with brine, dried over anhydrous Na_2SO_4 and evaporated in a vacuum to afford the corresponding crude products. The pure products were obtained by recrystallization from EtOH.

2,6-Dicyano-3-(4-methyloxycarbonylphenyl)-5-phenylaniline (7a): yellow powder; mp 274−275 °C; ^{1}H NMR (DMSO-d_6) δ 8.12 (d, J = 7.51 Hz, 2H), 7.83 (d, J = 7.57 Hz, 2H), 7.67 (m, 2H), 7.56 (m, 3H), 6.92 (bs, 2H), 6.88 (s, 1H), 3.93 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6) δ 166.2, 154.5, 150.5, 149.0, 142.3, 137.8, 130.8, 129.9, 129.8, 129.5, 129.1, 129.0, 118.9, 116.3, 116.1, 95.2, 94.4, 52.8 ppm; IR (KBr) ν 3396, 2922, 2214, 1725, 1621, 1300, 1122, 694 cm^{-1}; MS (EI) *m/z* 353 (M$^+$, 44.61); 57 (100); HRMS (EI) calcd for $C_{22}H_{15}N_3O_2$ (M$^+$) 353.1159, found 353.1158.

2,6-Dicyano-3-(4-methyloxycarbonylphenyl)-5-methylaniline (7d): yellow powder; mp 230−231 °C; ^{1}H NMR (CDCl$_3$) δ 8.16 (d, J = 8.25 Hz, 2H), 7.60 (d, J = 8.25 Hz, 2H), 6.73 (s, 1H), 5.28 (bs, 2H), 3.96 (s, 3H), 2.56 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$) δ 166.7, 152.8, 149.0, 148.3, 142.0, 131.3, 130.3, 128.7, 120.5, 115.9, 115.4, 97.5, 94.1, 52.6, 21.7 ppm; IR (KBr) ν 3477, 3357, 2920, 2221, 1720, 1647, 1295, 1109, 712 cm^{-1}; MS (EI) *m/z* 291 (M$^+$, 72.69), 260 (100); HRMS (EI) calcd for $C_{17}H_{13}N_3O_2$ (M$^+$) 291.1002, found 291.1002.

2,6-Dicyano-3-(4-methyloxycarbonylphenyl)-4-methyl-5-ethylaniline (7h): yellow crystal; mp 177−178 °C; ^{1}H NMR (DMSO-d_6) δ 8.08 (d, J = 8.14 Hz, 2H), 7.45 (d, J = 8.14 Hz, 2H), 6.49 (bs, 2H), 3.90 (s, 3H), 2.81 (q, J = 7.42 Hz, 2H), 1.86 (s, 3H), 1.16 (t, J = 7.45 Hz, 3H) ppm; ^{13}C NMR (DMSO-d_6) δ 166.3, 153.0, 151.5, 149.6, 143.4, 130.2, 129.9, 129.5, 122.7, 116.10, 116.07, 97.1, 95.5, 52.8, 26.7, 15.8, 13.9 ppm; IR (KBr) ν 3451, 3368, 2926, 2218, 1724, 1647, 1277, 767 cm^{-1}; MS (EI) *m/z* 319 (M$^+$, 100%); HRMS (EI) calcd for $C_{19}H_{17}N_3O_2$ (M$^+$) 319.1315, found 319.1316.

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Supporting Information Available: Reaction condition optimization. Experimental procedures. Spectral data for other products. Copies of ^{1}H and ^{13}C NMR spectra for all products. UV−vis absorption and fluorescence spectra for compounds **4p** and **4u**. X-ray structure details for compound **4c** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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