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Photocondensation in polycrystalline mixtures of arylacetic acids and 1,2,4,5-tetracyanobenzene

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Abstract

Irradiation of simple polycrystalline mixtures (1:1 molar ratios) of phenylacetic acids, such as 4-tolylacetic acid and 4-methoxyphenylacetic acid, and 1,2,4,5-tetracyanobenzene caused decarboxylations followed by dehydrocyanating condensation to give monobenzyltricyanobenzenes and dibenzyldicyanobenzenes. In the case of a polycrystalline mixture of 9-fluorenecarboxylic acid and tetracyanobenzene, the decarboxylation product 9-fluorene was obtained as the main product. The reactions proceed at the interface of the component crystallites. The product selectivities were different from those of the solution reactions.

Keywords: Photocondensation; Polycrystalline mixtures; Arylacetic acids; 1,2,4,5-Tetracyanobenzene

1. Introduction

A large number of photoinduced electron transfer (PET) reactions between donors and acceptors in solutions have been studied [1–3]. Photodecarboxylations are well known as a PET reaction, in which acceptors such as acridine and dicyanonaphthalene are used [4–6]. Tsujimoto et al. reported in a preliminary communication the photodecarboxylation of aliphatic carboxylic acids with tetracyanobenzene (**2**) in acetonitrile [7]. We already reported that several simple polycrystalline mixtures of two different substances such as *trans*-stilbene and carbazole [8] had photoreactivities and the reaction proceeded at the interface of the component crystallites [9–11]. We describe here that the mixed crystals prepared by evaporating the solutions of arylacetic acids (**1a–1d**) and **2** are also simple polycrystalline mixtures, that the irradiation causes decarboxylation and that the product selectivities are different from those in solution photoreactions.

2. Experimental details

2.1. General procedure

^{1}H nuclear magnetic resonance (NMR) spectra were measured on a 60 MHz JEOL spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer and a JASCO FT/IR-8300 spectrophotometer. UV and fluorescence spectra were measured on a Shimadzu UV-3100 spectrophotometer and RF-5000 spectrofluorophotometer respectively. Powder X-ray diffractograms were taken on a Rigaku Geigerflex by using an X-ray tube with a Cu target and equipped with an RAD-C system. Differential scanning calorimetry (DSC) was performed on a Rigaku Thermoflex TAS-200 DSC8230D and melting points (MPs) were not corrected. Elemental analysis was determined with a Yanaco CHN Corder MT-5. High performance liquid chromatography (HPLC) was used for determining the products on a Waters HPLC system with a photodiode array detector. All the reagents were commercially available.

2.2. Solid state photoreactions

Mixed crystals were prepared by dissolving 1:1 molar mixtures of arylacetic acids and tetracyanobenzene in

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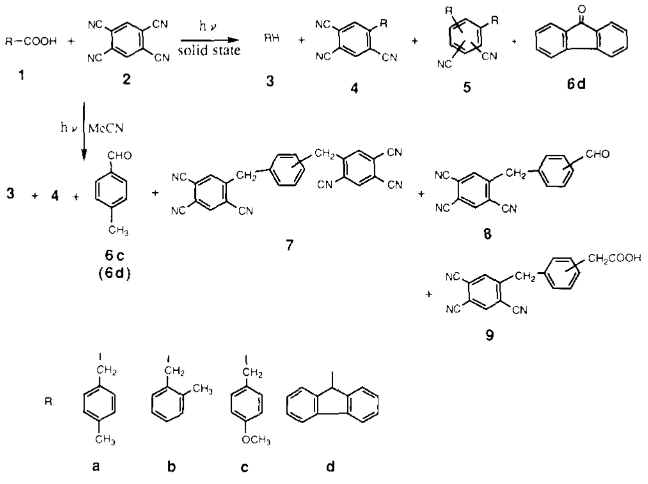
acetonitrile followed by evaporating the solvent to dryness and were pulverized to fine powder in a mortar. The mixed crystals were characterized by powder X-ray diffraction (PXD), DSC, IR, UV and fluorescence spectrometry. 20 mg of the mixed crystal was placed between two Pyrex glass plates and irradiated with a 400 W high pressure mercury lamp under argon at 15 °C for 24 h. The irradiated sample was methylated with diazomethane and analysed by HPLC (C_{18} column, methanol–water). The results are shown in Scheme 1 and Table 1.

2.3. *Preparatory photoreactions in solution*

For a common procedure, a solution of **1a**–**1d** (5 mmol) and **2** (5 mmol) in 100 ml of acetonitrile was internally irradiated with a 100 W high pressure mercury lamp under argon at room temperature. The reaction mixture was submitted to adequate separation methods such as filtration and preparative thin layer chromatography (TLC) (silica gel plate). The results are summarized in Scheme 1 and Table 2.



Scheme 1.

Table 1
Solid state photoreactions of arylacetic acids and tetracyanobenzene

Mixed crystal	Yield based on consumed **1** (%)				Conversion (%)	
	3	**4**	**5**[a]	**6**	**1**	**2**
1a–2	ND	4	10	–	94	13
1b–2	ND	9	10	–	87	25
1c–2	ND	8	10	–	100	44
1d–2	80	4	–	18	11	0.5

[a] The total yield of disubstituted *o*-, *m*- and *p*-isomers with respect to the R substituents is an estimated value by HPLC analysis.
ND, not detected.

2.3.1. *4-tolylacetic acid (**1a**) with **2***

Irradiation of a solution containing **1a** (750 mg) and **2** (891 mg) for 4 h followed by concentration and filtration of the reaction mixture gave 900 mg of **4a** as white solids: MP 182.0–185.0 °C (from MeCN); ^1H NMR (CD_3CN) δ 8.20 (s, 1H), 7.87 (s, 1H), 7.12 (s, 4H), 4.22 (s, 2H), 2.28 (s, 3H); IR (KBr) 3100, 3040, 2910, 2235, 1602, 1540, 1486, 1380, 1273, 930, 910, 830, 792 cm^{-1}; UV, λ_{max}(MeCN) 220.5 (log ϵ 4.80), 248.4 (4.26), 309.4 nm (3.53). Analysis calculated for $C_{17}H_{11}N_3$: C, 79.36%; H, 4.31%; N, 16.33%. Found: C, 79.64%; H, 4.68%; N, 16.03%. The filtrate was submitted to preparative TLC (6:1, benzene–ethyl acetate as an eluent) to give a further 100 mg of **4a** and 66 mg of **7a** as white needles: MP 274–277 °C (from dimethyl sulfoxide (DMSO)–MeOH, 1:1); ^1H NMR (DMSO-d_6) δ 8.67 (s, 2H), 8.30 (s, 2H), 7.34 (s, 4H), 4.35 (s, 4H); IR (KBr) 3100, 3040, 2920, 1597, 1508, 1486, 1380, 1270, 926, 850, 780 cm^{-1}; UV λ_{max}(MeCN) 220.2 (log ϵ 5.05), 245.0 (4.57), 309.8 nm (3.89). Analysis calculated for $C_{26}H_{12}N_6$: C, 76.46%; H, 2.96%; N, 20.58%. Found: C, 76.05%; H, 3.26%; N, 20.08%. The recovery of **2** was 1%.

2.3.2. *2-tolylacetic acid (**1b**) with **2***

After irradiation of **1b** (750 mg) and **2** (891 mg) in acetonitrile for 6 h, the reaction mixture was submitted to preparatory TLC (benzene–ethyl acetate, 5:1 as an eluent) to give **4b**, **7b**, **8b** and **9b**. **4b**: 569 mg, white crystals, MP 170.0–172.0 °C (from MeCN); ^1H NMR ($CDCl_3$ δ 8.05 (s, 1H), 7.40 (s, 1H), 7.00–7.34 (m, 4H), 4.30 (s, 2H), 2.20 (s, 3H); IR (KBr) 3100, 3035, 2940, 2920, 2230, 1596, 1540, 1488, 1454, 1375, 936, 908, 740 cm^{-1}; UV λ_{max}(MeCN) 220.5 (log ϵ 4.84), 249.7 (4.26), 309.5 nm (3.60). Analysis calculated for $C_{17}H_{11}N_3$: C, 79.36%; H, 4.31%; N, 16.33%. Found: C, 79.66%; H, 4.51%; N, 16.39%. **7b**: 155 mg, MP 208.0–209.0 °C (from DMSO–MeOH, 1:2); ^1H NMR (DMSO-d_6) δ 8.70 (s, 2H), 7.87 (s, 2H), 7.00–7.43 (m, 4H), 4.37 (s, 4H); IR (KBr) 3100, 3040, 2920, 2235, 1598, 1540, 1488, 1400, 1380, 908, 758 cm^{-1}; UV λ_{max}(MeCN) 220.3 (log ϵ 5.05), 248.4 (4.50), 299.0 (3.79) 309.7 nm (3.87). Analysis calculated for $C_{26}H_{12}N_6$: C, 76.46%; H. 2.96%; N, 20.58%. Found: C, 76.05%; H, 3.26%; N, 20.08%. **8b**: 6 mg, MP 169.0–172.0 °C (from MeOH); ^1H NMR ($CDCl_3$) δ 8.90 (s, 1H), 8.00 (s, 1H), 7.20–7.90 (m, 5H), 4.65 (s, 2H); IR (KBr) 3112, 3042, 2740, 2239, 1697, 1600, 1575, 1493, 1451, 1200, 1190, 906, 892, 868, 780, 767, 660 cm^{-1}. **9b**: 17 mg. This compound was isolated after methylation by using CH_2N_2; MP 86.5–89.0 °C (from MeOH); ^1H NMR (CD_3CN) δ 8.20 (s, 1H), 7.53 (s, 1H), 6.90–7.27 (m, 4H), 4.30 (s, 2H), 3.60 (s, 2H), 3.53 (s, 3H); IR (KBr) 3110, 3040, 2964, 2238, 1740, 1599, 1545, 1490, 1444, 1430, 1255, 1011, 937, 906, 842, 749 cm^{-1}. Analysis calculated for $C_{19}H_{13}N_3O_2$: C, 72.37%; H, 4.16%; N, 13.33%. Found: C, 72.25%;

Table 2
Isolated yields in the photoreactions of arylacetic acids with tetracyanobenzene in acetonitrile

Mixture	Irradiation time (h)	Yield based on consumed **1** (%)						Conversion (%)	
		3	**4**	**6**	**7**	**8**	**9**	**1**	**2**
1a–2	4	ND	78	–	3	–	–	100	99
1b–2	6	ND	46	–	8	0.5	1	97	77
1c–2	24	ND	46	10	–	–	–	78	36
1d–2	4	44	22	3	–	–	–	100	42

ND, not detected.

H, 4.37%; N, 13.20%. The recoveries of **1b** and **2** were 3% and 23% respectively.

2.3.3. *4-methoxyphenylacetic acid (1c) with 2*

After irradiation of **1c** (831 mg) and **2** (891 mg) in acetonitrile for 24 h, 477 mg of **2** was recovered by crystallization from acetonitrile–benzene (1:2). Next, the unreacted **1c** was removed with preparatory TLC (1,4-dioxane–hexane, 2:1 as an eluent) and other fractions were submitted to preparatory HPLC (C_{18} column, MeOH–H_2O, 3:2, as an eluent) to give 478 mg of **4c** as white crystals; MP 145.5–146 °C (from MeCN); ^{1}H NMR (acetone-d_6) δ 8.47 (s, 1H), 8.10 (s, 1H), 7.25 (d, $J=8.5$ Hz, 2H), 6.58 (d, $J=8.5$ Hz, 2H), 4.30 (s, 2H), 3.77 (s, 3H); IR (KBr) 3120, 3040, 2940, 2845, 2235, 1608, 1580, 1508, 1484, 1464, 1250, 1174, 1108, 1034, 938, 920, 852, 840, 797, 768 cm^{-1}; UV λ_{max}(MeCN) 219.2 (log ϵ 4.75), 249.8 nm (4.22). Analysis calculated for $C_{17}H_{11}N_3O$: C, 74.71%; H, 4.06%; N, 15.38%. Found: C, 74.41%; H, 4.25%; N, 15.42%. HPLC determination for the reaction mixture gave 36% yield of **4c** and 8% yield of **6c** at the conversions of 78% and 36% of **1c** and **2**, respectively.

2.3.4. *9-fluorenecarboxylic acid (1d) and 2*

After irradiation of a solution of **1d** (1050 mg) and **2** (891 mg) for 4 h, evaporation of the solution followed by the filtration afforded 495 mg (29% yield) of yellow crystals, which was a 1:1 charge transfer (CT) complex of fluorene **3d** and **2**: MP 250.0 °C (from MeCN), ^{1}H NMR (CD_3CN) δ 8.38 (s, 2H), 7.17–7.90 (m, 8H), 3.87 (s, 2H); IR (KBr) 3090, 3030, 2235, 1489, 1480, 1448, 1408, 1274, 1186, 920, 746 cm^{-1}; UV λ_{max}(MeCN) 209.6 (log ϵ 4.86), 217.8 (4.87), 222.8 (4.94), 255.8 (4.56), 264.0 (4.54), 300.0 (4.03), 316.0 nm (3.61), 380.8 (CT band). Analysis calculated for $C_{23}H_{12}N_4$: C, 80.22%; H, 3.51%; N, 16.27%. Found: C, 80.49%; H, 3.70%; N, 16.36%. The filtrate was submitted to preparatory TLC (benzene as an eluent) to give 133 mg of **3d**, 348 mg of **4d** as white crystals, 28 mg of **6d** and 258 mg of the starting **2** and no **1d** was recovered. **4d**: MP 271.3–272.5 °C (from MeCN–tetrahydrofuran, 2:1 by volume); ^{1}H NMR (CD_3CN) δ 8.27 (s, 1H), 7.80–8.00 (m, 2H), 7.23–7.57 (m, 7H), 5.57 (s, 1H); IR (KBr), 3095, 3030, 2220, 1592, 1490, 1475, 1448, 918, 756, 744 cm^{-1}; UV λ_{max}(MeCN) 217.4 (log ϵ 4.88), 265.6 nm (4.67). Analysis calculated for $C_{22}H_{11}N_3$: C, 83.27%; H, 3.49%; N, 13.24%. Found: C, 83.34%; H, 3.74%; N, 13.29%. **3d** and **6d**: the MPs and ^{1}H NMR, IR and UV spectral data were identical to those of an authentic sample.

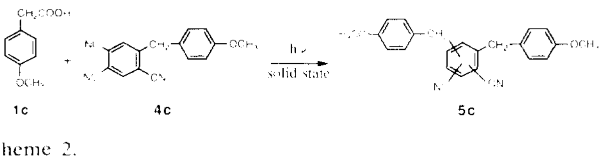
2.4. *Solid state photoreaction of 1c with 4c*

The 1:1 pulverized mixture (20 mg) of **1c** and **4c** was irradiated with a 400 W high pressure mercury lamp under argon at 15 °C for 5 h followed by HPLC analysis (Scheme 2).

2.5. *Crystallographic analysis of the products*

Data of **4c**: $C_{17}H_{11}N_3O$, MW = 273.29, monoclinic, $a=14.911(3)$ Å, $b=9.885(1)$ Å, $c=10.135(1)$ Å; $\beta=95.08(3)°$, $U=1466.6(4)$ Å^3, $\rho_{calc}=1.283$ g cm^{-3}; $\mu=0.80$ cm^{-1}; $Z=4$ in space group $P2_1/a$. 3336 reflections with $2\theta \leqslant 50.0°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo Kα radiation. Of these, 1289 with $I > 2\sigma(I)$ were judged as observed. The structure was solved using SHELX-86 [12]. Full-matrix least-squares refinement with anisotropic temperature factors for hydrogen atoms and isotropic hydrogens converged to $R=0.061$ and $R_W=0.025$ [13]. $(\Delta/\sigma)_{max}=0.31$, $\Delta\rho_{max}=0.49e$ Å^{-3}, $\Delta\rho_{min}=-0.46e$ Å^{-3}. All bond distances and angles agree well with generally accepted values. The molecular structure is shown in Fig. 1.

Data of **4d**: $C_{22}H_{11}N_3$, MW = 317.35, monoclinic, $a=18.979(2)$ Å, $b=12.047(2)$ Å, $c=7.211(4)$ Å; $\beta=95.08(3)°$, $U=1642.3(8)$ Å^3; $\rho_{calc}=1.283$ g cm^{-3}; $\mu=0.78$ cm^{-1}; $Z=4$ in space group $P2_1/a$. 3153 reflections with $2\theta \leqslant 50.0°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo Kα



Scheme 2.

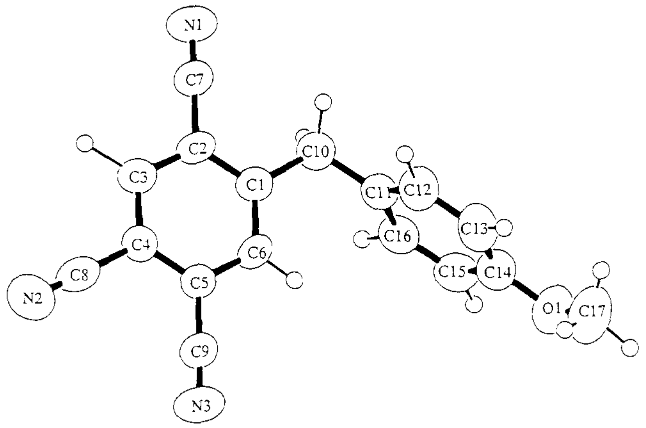


Fig. 1. An ORTEPII [15] drawing of 4c.

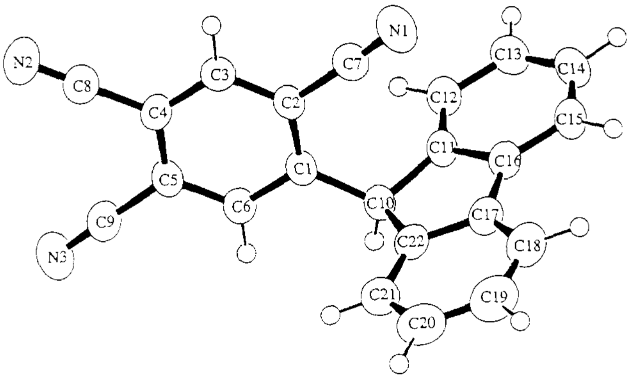


Fig. 2. An ORTEPII [15] drawing of 4d.

radiation. Of these, 2405 with $I>2\sigma(I)$ were judged as observed. The structure was solved using SHELX-86 [12]. Full-matrix least-squares refinement with anisotropic temperature factors for hydrogen atoms and isotropic hydrogens converged to $R=0.038$ and $R_W=0.032$ [13]. $(\Delta/\sigma)_{max}=0.01$, $\Delta\rho_{max}=0.15\,e\,\text{Å}^{-3}$, $\Delta\rho_{min}=-0.15\,e\,\text{Å}^{-3}$. All bond distances and angles agree well with generally accepted values. The molecular structure is shown in Fig. 2.

For both structures, atomic coordinates, bond distances and angles, and dihedral angles data have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The 1:1 mixed crystals of **1a**–**1d** and **2** prepared by evaporating the equimolar solutions in acetonitrile were the simple polycrystalline mixtures of each component, because new peaks did not appear in their PXD diagrams and IR spectra. Another preparation method of the mixed crystals by resolidifying the melt [9–11] was not adequate due to the thermal decomposition. The mixed crystals pulverized in mortars were placed between two Pyrex glass plates and irradiated with a 400 W high pressure mercury lamp under argon at 15 °C for 24 h followed by methylation with diazomethane and HPLC analysis. The results are shown in Scheme 1 and Table 1.

Irradiation of the 1:1 mixed crystal between the phenylacetic acid derivatives **1a**–**1c** and **2** gave similar photoproducts, monosubstituted products **4a**–**4c** and the disubstituted products **5a**–**5c**, the latter of which were the mixtures of *o*-, *m*- and *p*-isomers with respect to the R substituents and the ratios were determined to be 1:7:2 by the ^{1}H NMR integration. However, separation of each isomer was difficult because of the near retention times in preparatory HPLC separation. It was confirmed that **5c** was produced by the reaction of **4c** with **1c** (Scheme 2); the 1:1 pulverized mixture of **1c** and **4c** was irradiated for 5 h in the solid state to give **5c** in 10% yield based on the consumed **1c** at 78% and 49% conversions of **1c** and **4c** respectively and the ratio of *o*-, *m*- and *p*-isomers was also 1:7:2. This result indicates that **4c** which was produced at the interface of the component crystallites reacted again with **1c** to give **5c**. It is coincident with the result that almost constant yields, 8%, 9% and 7% respectively, were obtained by the irradiation of the mixed crystal of **1c** and **2** for 2 h, 6 h and 24 h. At these irradiation times 64%, 86% and 100% conversions of **1c** and 27%, 30% and 44% conversions of **2** respectively were observed. The decarboxylation products, *p*-xylene (**3a**), *o*-xylene (**3b**) and 4-methoxytoluene (**3c**), were not detected. It may be due to the loss of the volatile products **3a**–**3c** during the irradiation and product separation processes. The low material balances in the photoreaction of the three mixed crystals of **1a**–**1c** and **2** may be caused by the loss of **3a**–**3c** and the polymerization of the substrates. The solid state photoreaction of the mixed crystal of 9-fluorenecarboxylic acid (**1d**) and **2** gave 9-fluorene (**3d**) in high yield as the decarboxylation product probably because **3d** is non-volatile (MP 115 °C), different from **3a**–**3c**.

For a comparison solution photoreactions of **1a**–**1d** with **2** in acetonitrile were also carried out in a preparatory scale (Scheme 1 and Table 2). Monosubstituted products **4a**–**4d** were obtained as the major product. However, under condition of a large excess of acid (100 times) with **2** in the work of Tsujimoto et al. [7] the disubstitution probably occurs in acetonitrile. The molecular structure of 2,4,5-tricyanophenyl-4′-methoxyphenylmethane (**4c**) was confirmed by X-ray crystallographic analysis as shown in Fig. 1. The dihedral angle between two benzene rings is 91.6° and the torsion angles of C2–C1–C10–C11 and C1–C10–C11–C12 are 171.1(4)° and −86.8(5)° respectively. The molecular structure of 9′-fluorenyl-2,4,5-tricyanobenzene (**4d**) is shown in Fig. 2. 2,4,5-tricyanobenzene and fluorene rings are coplanar within 0.007(2) Å respectively, and the dihedral angle of these planes is 98.3°. The torsion angles of C2–C1–C10–C11 and C5–C1–C10–C22 are −45.1(2)° and −116.7(1)° respectively. The products **7a** and **7b** which were not produced in the solid state photoreactions were obtained by the solution reaction, different from the solid state reaction. In the photoreaction of **1d** with **2** in acetonitrile, a 1:1 yellow CT complex of **3d** and **2** precipitated which had the melting point at 250 °C and the CT band at 381 nm in acetonitrile. This CT complex had no photoreactivity in the solid state.

Quantum yields in the solid state were determined by the procedure reported by Ito et al. [14]. The crystalline thin film was prepared by the addition of a small amount of acetone (0.5 ml) containing **1a** (0.05 mmol) and **2** (0.05 mmol) in a Pyrex tube (180×17 mm inner diameter) and by the evaporation of the solvent with a vacuum rotary evaporator. The film was irradiated on a merry-go-round apparatus with a 400 W high pressure mercury lamp through a potassium chromate filter (light transmission, 300–330 nm and more than 450 nm) under argon at 15 °C. The irradiation was stopped at a small conversion (less than 10%) and the products formed were analysed by HPLC. The photocyclization reaction of 2,4,6-tri-isopropylbenzophenone in benzene ($\Phi_{\mathrm{CB}}=0.52$) was used as an actinometer. Quantum yields for the reactions in acetonitrile solution containing 0.005 M **1a** and 0.005 M **2** were also measured simultaneously with the usual merry-go-round technique. The quantum yields obtained were 0.04 and 0.20 in the solid and in the solution respectively.

We measured fluorescence spectra of the mixed crystals and their components with the front face arrangement as shown in Table 3. In all cases, the fluorescence spectra of the mixed crystals were approximately the same as the sum of those of the components with lower emission intensities. In the fluorescence spectra of the mixed crystals **1a–2** and **1b–2**, new peaks at 457 nm and 428 nm respectively appeared. The appearance of these new peaks indicates that an excimer may be formed at the interface of the component crystallites. It should be noted that the fluorescence behaviour of the present mixed crystals is different from the facile energy transfer at the interface of the mixed crystals between NH-heteroaromatics and arenes as already reported [9,11], such as indole–phenanthrene and indole–*trans*-stilbene mixed crystals.

Table 3
Fluorescence spectral data of the mixed crystals of arylacetic acids and tetracyanobenzene and the components

Mixed crystal and component	Fluorescence maximum [a] (nm)
4-tolylacetic acid **1a**	292, 359
2-tolylacetic acid **1b**	287, 360
4-methoxyphenylacetic acid **1c**	303, 360
9-fluorenecarboxylic acid **1d**	332, 396(sh), 421(sh)
Tetracyanobenzene **2**	337, 346, 362, 378
Mixed crystal **1a**–**2**	289, 335, 346, 362, 378, 457
Mixed crystal **1b**–**2**	284, 335, 346, 362, 428
Mixed crystal **1c**–**2**	299, 336, 347, 361, 377
Mixed crystal **1d**–**2**	333, 347, 360, 378(sh)

[a] Excitation at 275 nm.

In conclusion, the solid state photodecarboxylation of the simple polycrystalline mixtures between arylacetic acids and tetracyanobenzene occurs at the interface of the component crystallites with different product selectivities from those in the solution photoreactions.

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