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Fluorescent Cyanoacrylate Monomers and Polymers for Fingermark Development

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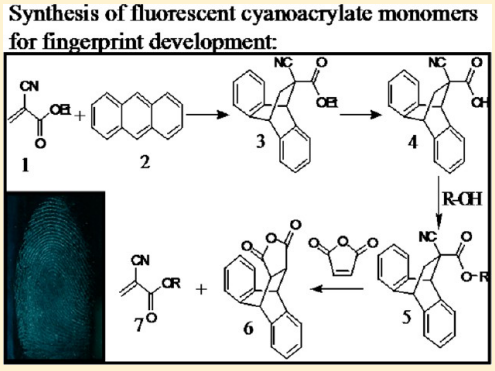
ABSTRACT: Cyanoacrylate esters with fluorescent side groups were synthesized and tested as agents for latent fingerprint development. Reactive monomers with benzyl, anthracyl, naphthyl, fluorenyl, propagyl, and cyanomethyl side groups were synthesized using the formation of an ethyl cyanoacrylate, anthracene adduct, followed by hydrolysis of the ethyl ester to the acid and esterification with a desired alcohol, and finally release of the monomer by retro-Diels–Alder with maleic anhydride. Monomers were prepared in high yield and purity as determined by spectral analysis. Attempts to synthesize these monomers from poly(ethyl cyanoacrylate) by trans-esterification and depolymerization resulted in low yields and low purity. The synthesized fluorescent monomers were found to be effective for latent fingerprint development in solution forming clear fluorescent fingerprint images suitable for forensic fingerprint comparison. These monomers can complement the current use of the commonly used nonfluorescent ethyl cyanoacrylate monomers for fingerprint development.



1. INTRODUCTION

Alkyl cyanoacrylates are solvent free liquids that polymerize and cure rapidly in the presence of nucleophiles (including moisture from the air) to form adhesive, glue, and films.[1,2] These alkyl cyanoacrylates have long been used for bonding nonporous materials in biomedical fields such as tissue adhesives, for drug delivery, in the automobile and electronics industries, and in forensic laboratories for fingerprint development.[3,4] Earlier generations of cyanoacrylates (methyl, ethyl) had significant performance limitations such as poor thermal stability, peel strength, and high tissue reaction. Continued research on cyanoacrylates resulted in the development of new alkyl cyanoacrylates to overcome these limitations. Cyanoacrylate butyl and octyl esters have been found to be biodegradable and biocompatible.[5−7] Cyanoacrylate ethyl ester has been used as an adhesive for nonmedical applications by applying the monomer, which is rapidly polymerized into a strong adhesive polymer. This monomer, commonly known as "Superglue", has been used extensively as a fingerprint developer; latent fingerprints on exhibits are discovered when applying "Superglue" vapors in a closed chamber. Fingerprint components polymerize the monomer so that a white print is visualized. Its success as a method of choice lies in the fact that it may be applied to a large variety of surfaces such as plastics, metal, and glass. Cyanoacrylates are nonselective in their compound target and are therefore able to develop fingerprint residue with both eccrine and sebaceous.[3−5] This method can be used on older as well as recent fingerprints. One of the limitations of its use is that due to its white color formation, sometimes the developed fingerprints are only slightly visible. One has to use a visible or fluorescent dye to enhance visibility of the developed fingerprints. An additional problem is that overdeposition of cyanoacrylate polymerization on a latent fingerprint may cover the print precluding forensic comparison. In addition, the application of a dye as a second step is time-consuming and not cost-effective in field development of prints. Many experiments have been conducted in which physical mixtures of fluorescent dyes and cyanoacrylate monomers were fumed together and deposited onto fingerprint.[8,9] The sublimated state is supposed to react with one or more of the components of the residue of a latent fingerprintto form a discernible fluorescent image of the mark. Despite these efforts, mixing large amounts of fluorescent dyes into the cyanoacrylate monomer resulted in poor fluorescence prints without practical utility. To the best of the authors' knowledge, no cyanoacrylate monomers other than alkyl derivatives have been reported for fingermark applications, despite Rao's work.[10] Furthermore, fluorescent cyanoacrylate monomers have not been reported in the scientific literature.

In an effort to synthesize new cyanoacrylates that would contain colored, fluorescent, or UV absorbing groups, the authors successfully synthesized cyanoacrylate esters that show the desired properties. Several cyanoacrylate esters with fluorescent moiety were synthesized and tested for fingermark development. The use of cyanoacrylates in solution was

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suggested by Mr. Itoh, a forensic technician in Japan.[11] With this in mind, the authors applied the newly synthesized cyanoacrylates in solution.

2. EXPERIMENTAL SECTION

2.1. Materials. Reagents and deuterated solvents for NMR spectrography were purchased from Sigma-Aldrich Israel (Rehovot, Israel). The ethyl cyanoacrylate (ECA) used was manufactured by Loctite and commercialized as Hard Evidence by Lightning Co. (Jacksonville, FL). By-40 was purchased from W.S. Simpson & Co. (London, U.K.). All reagents and compounds used for synthesis were purchased from Sigma-Aldrich (Rehovot, Israel). Analytical grade solvents were bought from Biolab (Jerusalem, Israel). Silica gel for thin layer chromatography (TLC) and liquid chromatography (LC) was purchased from Merck (Damstart, Germany). NMR was recorded on a Varian instrument at 300 MHz for proton and 74 MHz for ^{13}C spectra. Chemical shifts are expressed in ppm. FT-IR was recorded on a Bruker instrument as a film on NaCl window. ESI-MS was recorded on a ThermoQuest Finnigan LCQ-Duo instrument. Fingermark development at atmospheric pressure was performed with a standard Superglue chamber manufactured for the Israel Police by "Automat Ltd." (Jerusalem, Israel). Vacuum superglue was performed in a cylindrical aluminum chamber attached to a rotary oil pump, both from Edwards High Vacuum Int. (Crawley, U.K.). Microscopic observations were performed on an Olympus BX60 instrument equipped with a reflected light fluorescence attachment.

2.2. Methods. *2.2.1. Synthesis. Ethyl Cyanoacrylate–Anthracene Adduct (**3**).* Anthracene (3 g, 16.83 mmol) was dissolved in toluene (30 mL) in a nitrogen atmosphere. Boric acid (5.4 mg, 0.51 mol %) and catechol (40.8 mg, 2.20 mol %) were added, followed by ethyl cyanoacrylate (2.95g, 23.57 mmol). The mixture was refluxed for 18 h and monitored by TLC (20% Ethyl acetate/hexane). Toluene was evaporated under reduced pressure, and the gum was passed through silica gel column eluting with hexane followed by dichloromethane (0–100%) to obtain a 3.7 g white solid; that solid was suspended in diethyl ether 10 mL and filtered through suction to get a 3.57 g pure ester adduct in 70% yield. Anal. (Found) Calcd: C, (79.19) 78.82; H (5.65) 5.53; N (4.62) 4.62.

^1H NMR (300 MHz, $CDCl_3$): δ 7.4(m, 1H), 7.3(m, 2H), 7.31–7.11 (m, 5H), 4.88(s, 1H), 4.43(t, 1H, J = 2–7), 4.16 (q, 2H), 2.8 (d, 1H, J = 2.7), 2.22(dd, 1H, J = 2.7) 1.3 (t, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): 167, 143.34, 142.68, 138.32, 137.43, 127.895, 127.84, 126.91, 126.65, 126.12, 125.38, 124.22, 123.92, 120.03, 63.53,52, 47, 43.37, 38.23. 14.39. Mass: 321(m + 18), 326 (m + 23), 179 (anthracene + 1); FT-IR: 2980 (alkyl CH stretch); 2255 (CN); 1770 (ester CO stretch); 1465 (C=C strecht); 1253 (ester stretch). MP: 124–125 °C. TLC: anthracene R_f 0.9, ethyl cyanoacrylate adduct R_f 0.69, ethyl cyanoacrylate polymer does not move on TLC.

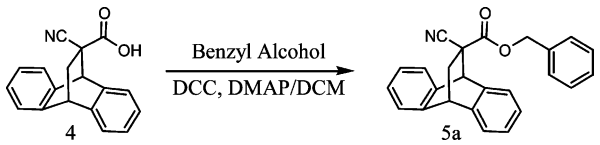
*Cyanoacrylic Acid–Anthracene Adduct (**4**).* Ethyl cyanoacrylate anthracene adduct (7.5 g, 24.72 mmol) was dissolved in THF (150 mL); dropwise 5% aqueous lithium hydroxide (31 mL) (1.55g, 37 mmol) was added and stirred overnight at 25 °C. TLC (20% ethyl acetate/hexane + 0.1% AcOH) showed completion of hydrolysis. Tetrahydrofuran (THF) was evaporated under reduced pressure, and the reaction mixture was cooled to 10 °C, acidified by dil. HCl to pH 2. It was extracted with ethyl acetate (3 × 50 mL); Evaporation of ethyl acetate under reduced pressure gave a white solid, which was suspended in diethyl ether and filtered to obtain 6.21g pure acid (91%). Anal. (Found) Calcd: C, (78.53) 78.12; H, (4.77) 4.63; N, (5.09) 5.07.

^1H NMR (300 MHz, $CDCl_3$): δ 7.48 (m, 1H), 7.33 (m, 2H), 7.22–7.13 (m, 5H), 4.87 (S, 1H), 4.43 (d, 1H, J = 2.4), 2.7 (dd, 1H, J = 2.7, 10.5), 2.2 (dd, 1H, J = 3, 10.5). ^{13}C NMR: 170.3, 153.98, 142.91, 142.47, 137.91, 127.94, 127.89, 126.9, 126.74, 126.10, 125.47, 124.05, 123.86, 119.38, 51.82, 47.8, 43.28, 38.17. Mass: 298 (m + Na), 179 (anthracene + 1). Mp: 205–207 °C. FT-IR: 3400–2600 (OH stretch); 2243 (CN); 1718 (acid CO stretch); 1483 (C=C stretch). R_f (20% ethyl acetate/hexane + drop of acetic acid) = 0.3.

*Esters of Cyanoacrylic Acid–Anthracene Adduct (**5**).* Cyanoacrylic acid anthracene adduct (1.5 g, 5.44 mmol) was dissolved in dichloromethane (30 mL) in a dry round-bottom flask under nitrogen atmosphere. The desired alcohol (5.49 mmol) and 2 mg of dimethylaminopyridine (DMAP) as a catalyst were added. The solution was cooled to 0 °C, and a solution of dicyclohexylcarbodiimide (DCC) (1.132g, 5.49 mol) in dichloromethane (30 mL) was added dropwise. The reaction mixture was stirred for 8 h TLC (20% ethyl acetate/hexane + 0.1% acetic acid); monitoring shows completion of the reaction (consumption of starting acid adduct). The solution was filtered, washed with dichloromethane (30 mL). The solvent was evaporated under reduced pressure to yield a white solid, which was crystallized from diethyl ether to obtain pure esters (~90%).

*Cyanoacrylate Esters (**7**).* A clean, dry 100 mL round bottomed flask under nitrogen atmosphere was charged with cyanoacrylate ester–anthracene adduct (51 mmol), maleic anhydride (1.5 g, 153 mmol), dry xylene (50 mL), hydroquinone (15 mg), and phosphorus pentoxide (350 mg). The mixture was refluxed for 36 h, cooled to 10 °C, and filtered. The filtration cake was washed with diethyl ether and dried to yield 1.39g maleic anhydride anthracene adduct (98%). Solvents were evaporated from the mother liquor to leave syrup primarily containing the desired cyanoacrylate esters. The residue was crystallized from ether to afford a pure substance.

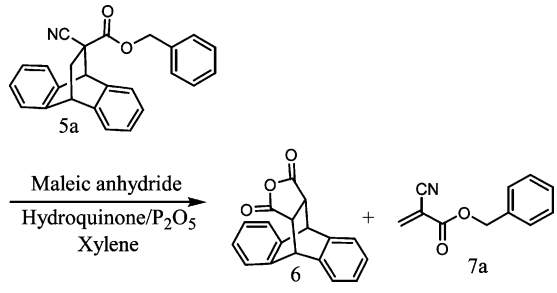
*Synthesis of Cyanoacrylate Benzyl Ester–Anthracene Adduct (**5a**).* Esterification of the cyanoacrylic acid–anthracene adduct (**4**) with benzyl alcohol by DCC coupling in dichloromethane (DCM)



In a clean and dry 500 mL round-bottomed glass charge under N_2 acid adduct (15 g, 54.47 mmol), DMAP (3 mg) and 300 mL of dichloromethane, followed by benzyl alcohol (5.72 mL, 55 mmol). The flask was immersed into an ice/water bath, and a solution of DCC (11.35g, 55 mmol) was added dropwise and stir for 6 h. TLC (20% ethyl acetate/hexane) shows completion of reaction (acid R_f = 0.3, ester R_f = 0.71). The white precipitate of dicyclohexyl urea was isolated by filtration and the filtrate was evaporated to dryness under reduced pressure to yield a white solid. The isolated solid was washed with diethyl ether to yield 18 g (90% yield) of the pure ester adduct.

^1H NMR (300 MHz, $CDCl_3$): δ 7.45(m, 3H), 7.3(m, 3H), 7.12 (m, 2H), 6.9 (t, 1H, J = 7.5), 6.8 (d, 1H, J = 7.2), 5.19 (d, 1H, J = 12), 5.06 (d, 1H, J = 12.3), 4.8 (S, 1H), 4.4 (S, 1H), 2.8 (dd, 1H J = 2.1 and 11.11), 2.2 (dd, 1H, J = 2.1. 11.1). ^{13}C NMR: 166.87, 143.18, 142.46, 138.11, 137.02, 134.87, 129.20, 129.12, 129.007, 127.8, 127.75, 126.87, 126.62, 126.07, 125.25, 124.03, 123.83, 119.97, 69.01, 51.95, 47.52, 43.33, 38.18. Anal (Found) Calcd: C, (82.17) 80.17; H, (5.24) 5.30; N, (3.83) 4.02. IR cm^{-1}: 3034, 2939, 2236, 1757, 1623, 1457, 1227, 1189, 1049, 966, 736, 698. Mp: 203–205 °C.

*Cyanaoacrylate Benzyl Ester (**7a**).* Retro-Diels–Alder reaction of adduct with maleic anhydride was applied as follows:



In a clean dry round-bottomed glass fitted with a reflux condenser, benzyl cyanoacrylate anthracene adduct (5 g, 13.67 mmol), maleic

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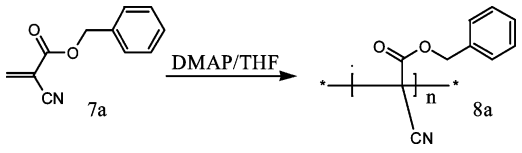
anhydride (4 g, 40.8 mmol), hydroquinone (15 mg), P_2O_5 (1 g), and dry xylene (150 mL) were loaded under nitrogen, and the reaction mixture was refluxed with vigorous stirring for 56 h. The reaction mixture was allowed to reach room temperature and filtered rapidly to remove unreacted maleic anhydride and maleic anhydride-anthracene adduct under inert atmosphere. The solution was evaporated to dryness, and the reddish brown solid residue was suspend in 100 mL dry diethyl ether, filter, and evaporated to about 10 mL and left under refrigeration overnight to allow isolation of a red oil as benzylcyanoacrylate monomers. Impurities confirmed by NMR are maleic anhydride, maleic anhydride-anthracene adduct and unreacted benzylcyanoacrylate anthracene adduct, accounting for 15% to 20%, crude weight to 2.7 g. The residue was further purified in dry ether.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31−7.33 (m, 5H), 7.08 (d, 1H, J = 0.6), 6.63 (d, 1H, J = 0.6H2), 5.34 (S, 2H); ^{13}C NMR: 160.4, 143.89, 140.94, 129.07, 129.015, 128.94, 116.6, 114.3, 68.75. IR, cm^{-1}: 3124, 2992, 2232, 1732, 1602.

*Synthesis of Poly(benzyl cyanoacrylate) (**8a**).* Benzyl cyanoacrylate monomer (2g, 10.68 mmol) was dissolved in dry THF, and



dimethyl aminopyridine (0.15 mg) was added and left for 4 h with stirring. The pinkish red suspension was filtered and washed with diethyl ether to yield 1.88g of polymer.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (bs-5H), 5.2 (bs, 2H), 2.3 (bs, 2H). IR, cm^{-1}: 2992, 2240, 1745, 1439, 1372, 1247, 1008, 856, 744, 691. GPC: M_w = 10982 Da. Differential scanning calorimetry (DSC): 362 °C.

Other cyanoacrylate ester monomers were synthesized using the above procedures; the data analysis is as follows:

*4-Nitrobenzyl Cyanoacrylate Anthracene Adduct (**5b**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2 (d, 2H, J = 8.2), 7.46 (d, 2H, J = 8.1), 7.43 (S, 1H), 7.3 (m, 2H), 7.21 (m, 3H), 6.9 (m, 2H), 5.19 (s, 2H) 4.8 (S, 1H), 4.4 (s, 1H), 2.8 (dd, 1H) 2.2 (dd, 1H). ^{13}C NMR: 166.85, 148.20, 143.08, 142.57, 141.87, 137.91, 137.05, 129.24, 127.96, 126.97, 126.65, 126.08, 125.13, 124.24, 124.175, 123.94, 119.75, 67.28, 52.0, 47.66, 43.22, 38.30. IR, cm^{-1}: 3077, 2950, 2243, 1754, 1630, 1605, 1516, 1453, 1340, 1270, 1245, 1226, 1194, 1106, 1055, 827, 769, 630,587; Mp: 149−151 °C. Anal. (Found) Calcd: C, (73.16) 72.86; H, (4.42) 4.63; N, (6.83) 6.98.

*4-Nitrobenzyl Cyanoacrylate (**7b**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 8.4 Hz), 7.13(d, 1H, J = 0.6 Hz), 6.71 (d, 1H, J = 0.6 Hz), 5.4 (S, 2H). ^{13}C NMR: 160.32, 144.67, 141.67, 141.65, 128.83, 124.26, 116.22, 114.33, 66.92. IR cm^{-1}: 3120, 2987, 2236, 1735, 1657, 1606, 1514, 1345, 1280, 1196, 994. mp: 85−87 °C. Mass: 232 (m+); Anal. (Found) Calcd: C, 56.86 (56.90); H, 3.58 (3.47); N, 11.91 (12.06).

*Cyanoethylcyanoacrylate Anthracene Adduct (**5c**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.538 (m, 1H), 7.35 (m, 2H), 7.33- 7.12 (m, 5H), 4.94 (s, 1H), 4.47 (t, 1H, J = 2.7), 4.29−4.13 (m, 2H), 2.84 (dd, 1H, J = 2.7) 2.64- 2.60 (m, 2H), 2.25 (dd, 1H, J = 2.7). ^{13}C NMR: 166.767, 143.01, 142.40, 137.71, 137.02, 128.04, 127.93, 126.99, 126.81, 126.19, 125.22, 124.29, 123.81, 119.39, 116.68, 61.29, 52.00, 47.52, 43.25, 38.22, 18.06.

*Cyanoethylcyanoacrylate Monomer (**7c**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (d, 1H, J = 0.6H2), 6.70 (d, 1H, J = 0.6H2), 4.47 (t, 2H, J = 6.3 Hz), 2.81 (t, 2H, J = 6.3 Hz). ^{13}C NMR: 160.19, 144.96, 116.53, 115.90, 114.19, 60.95, 18.06.

*Propargylcyanoacrylate Anthracene Adduct (**5d**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51−7.48 (m, 1H), 7.35−7.30 (m, 3H), 7.25−7.11 (m, 4H), 4.92 (S, 1H), 4.77−471 (dd, 1H, J = 2.7, 2.4), 4.64−4.58 (dd, 1H, J = 2.4), 4.43 (t, 1H, J = 2.7 and 2.4), 2.83−2.78 (dd, 1H, J = 2.7), 2.53 (t, 1H, J = 2.4) 2.26−2.20 (dd, 1H, J = 2.7). ^{13}C NMR: 166.41, 143.116, 142.44, 137.95, 136.95, 127.97, 127.89, 126.95, 126.71, 126.14, 125.60, 124.12, 123.87, 119.53, 76.60, 76.53, 54.53, 51.86, 47.37, 43.27, 38.27. IR, cm^{-1}: 3295, 3282, 2904, 2904, 2242, 2132, 1748, 1459, 1367, 1270, 1228, 1183, 1049, 754. Mp = 96−98 °C. Anal. (Found) Calcd: C, (80.43) 79.76; H, (4.82) 4.90; N, (4.47) 4.70.

*Propargylcyanoacrylate Monomer (**7d**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (S, 1H), 6.68 (s, 1H), 4.86 (d, 2H), 2.55 (t, 1H); ^{13}C NMR: 160.03, 144.56, 116.20, 114.25, 76.52, 76.38, 54.23

*Anthracenemethylcyanocrylate Anthracene Adduct (**5e**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.6 (S, 1H), 8.24 (d, 2H, J = 8.7), 8.10 (d, 2H, J = 8.1), 7.6 (t, 2H, J = 6.6, 8.7), 7.5 (t, 2H, J = 7.8), 7.30−7.11 (m, 5H), 7.0 (t, 1H, J = 8.4), 6.56 (t, 1H, J = 8.5), 6.4 (d, 1H, J = 12.6), 6.22 (d, 1H, J = 7.2), 5.94 (d, 1H, J = 12.3), 4.58 (S, 1H), 4.34 (t, 1H, J = 2.4), 2.86 (dd, 1H J = 2.6), 2.18 (dd, 1H, J = 2.6). ^{13}C NMR: 167.25, 143.24, 142.23, 137.99, 136.83, 131.63, 131.47, 130.10, 129.45, 127.72, 127.58, 127.33, 126.77, 126.29, 126.06, 125.62, 125.10, 124.14, 123.93, 123.72, 119.98, 61.56, 51.82, 47.60, 43.29, 38.18. IR, cm^{-1}: 3057, 3025, 2947, 2232, 1745, 1621, 1452, 1251, 1205, 1173, 1038, 865, 725. Mp = 160−162 °C. Anal. (Found) Calcd: C, (85.14) 85.00; H, (4.98) 4.98; N, (3.01) 3.07.

*Anthracenemethyl Cyanoacrylate (**7e**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4- 7.39 (m, 1H), 7.38−7.32 (m, 4H), 7.24−7.18 (m, 4), 7.06 (S, 1H), 6.72 (S, 1H), 5.64 (dd, 2H).

*Naphthylmethylcyanoacrylate Anthracene Adduct (**5f**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, 1H, J = 7.8), 7.9 (m, 2H), 7.65−7.58 (m, 4H), 7.47−7.37 (m, 2H), 7.74−7.06 (m, 3H), 7.06 (m, 1H), 6.78 (m, 1H), 6.38 (m, 1H), 5.65 (d, 1H, J = 12.3), 5.54 (d, 1H, J = 12.3), 4.68 (S, 1H), 4.38 (t, 1H, J = 2.4), 2.84 (dd, 1H, J = 2.7), 2.20 (dd, 1H, J = 2.7). ^{13}C NMR: 166.91, 143.15, 142.28, 138.03, 136.82, 134.02, 131.99, 130.41, 130.13, 129.09, 128.89, 127.37, 127.61, 127.27, 126.79, 126.49, 126.36, 126.04, 125.55, 125.05, 123.90, 123.81, 123.74, 119.96, 67.27, 51.88, 47.55, 43.28, 38.11. IR, cm^{-1}: 3019, 2960, 2239, 1751, 1626, 1459, 1219, 1186, 1037, 952. Mp: 155−158 °C. Anal. (Found) Calcd: C, (83.83) 83.71; H, (5.03) 5.05; N, (3.37) 3.44

*Naphthylmethylcyanoacrylate Monomer (**7f**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (m, 1H), 7.97−7.91 (m, 2H), 7.58−7.41 (m, 4H), 7.01 (s, 1H), 6.58 (s, 1H), 5.77 (S, 2H).

*Fluorenmethylcyanoacrylate Anthracene Adduct (**5g**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8 (d, 1H, J = 7.5), 7.66 (d, 1H, J = 7.7), 7.5−7.22 (m, 12H), 7.22−7.17 (m, 1H), 7.06−7.04 (m, 1H), 4.83 (s, 1H), 4.47 (m, 2H), 4.25 (m, 2H), 2.8 (dd, 1H), 2.23 {dd, 1H). ^{13}C NMR: 167.09, 143.41, 143.34, 143.07, 142.49, 141.59, 141.55, 138.09, 137.21, 128.35, 127.87, 127.65, 127.59, 126.91, 126.74, 126.13, 125.45, 125.33, 125.20, 124.11, 123.87, 120.44, 120.42, 119.87, 69.35, 52.12, 47.72, 46.86, 43.36, 38.32; IR, cm^{-1}: 3038, 2966, 2927, 2233, 1752, 1628, 1446, 1374, 1270, 1244, 1231, 1185, 1107, 1043, 965, 764, 582. Mp: 91−93 °C.

*Flurenmethylcyanoacrylate Monomer (**7g**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, 2H, J = 7.2), 7.68 (d, 2H, J = 7.2), 7.43−7.41 (m, 2H), 7.37−7.32 (m, 2H), 7.03 (d, 1H, J = 1.2), 6.68 (d, 1H, J = 1.7), 4.53 (m, 3H).

2.2.2. Development of Latent Fingerprints. Sebaceous and eccrine fingerprints were deposited by a single donor. Fresh fingerprints and 1 day old fingerprints were used. Sebaceous fingerprints were deposited by first rubbing the hands on oily parts of the forehead. Eccrine fingerprints were deposited after washing the hands thoroughly and letting the hands dry. After about 15 min, fingerprints were deposited. Those fingerprints deposited on microscope glass slides were developed in a small Superglue chamber, provided with a hot plate tuned to 200 °C. The slides were exposed to fumes in the chamber for 20 min, while heating synthesized cyanoacrylates. The fingerprint development power of these substances was also tested under vacuum. A Pyrex desiccator was used as a development chamber. The entire chamber was heated over a heating plate for two to 3 h while maintaining a vacuum (~10^{-4} mmHg).

2.2.3. Development of Fingerprints in Organic Solution. Cyanoacrylate monomers were added to inert organic solvents, chlorinated hydrocarbons, hydrocarbons, ethers, and aromatic solvents to determine solubility, stability, and ability to develop fingerprints applied on glass slides. Fingerprint development was determined by

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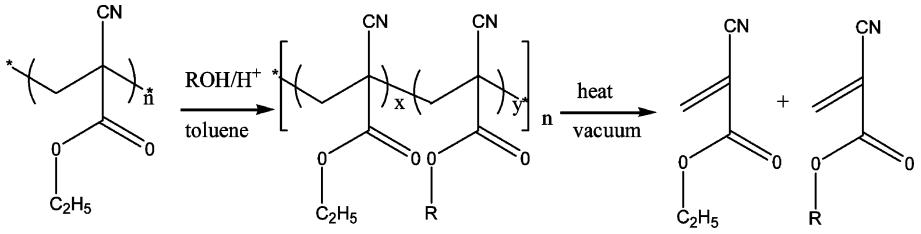
Scheme 1. Synthesis of Cyanoacrylate Esters by Depolymerization of Transesterified Polymers[a]



[a]R represents a fluorescent residue.

dipping glass slides containing latent fingerprints into the monomer solution for a few seconds; then the slides were dried in the hood at room temperature and visualized under appropriate light. Of the various solvents tried, xylene, dichloromethane (DCM), and ethyl acetate (EtOAc) fulfilled the primary requisites of dissolving the substances without polymerizing them and with minimal damage to the fingerprint. Xylene was selected at a concentration of 1% w/v. Xylene solution of known BY-40 fluorescent dye was used for comparison.

Fingermark results were photographed under incident white light. The results of the new materials were also photographed by penetrating UV illumination (350 nm) using a lens equipped with a standard UV filter. Fingermarks developed by BY-40 fluorescent dye + ECA were photographed under penetrating blue light (450 nm) with a lens equipped with an orange filter.

3. RESULTS AND DISCUSSION

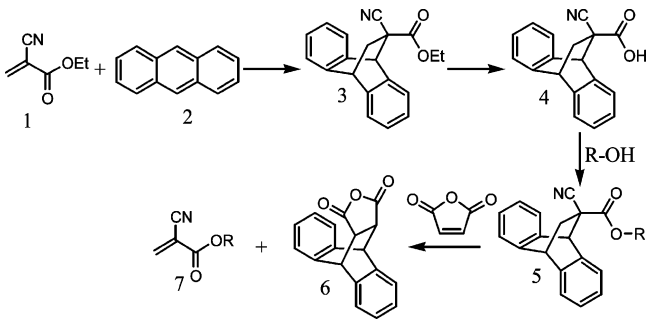
3.1. Synthesis of Monomers and Polymers. Two methods were applied for the synthesis of cyanoacrylate ester monomers. The first attempt (Scheme 1) to produce the monomers involved the trans-esterification of poly(ethyl cyanoacrylate).

A test was conducted to replace ethyl esters with fluorescent alcohols. The transesterification pathway toward polymer was thoroughly explored with benzyl alcohol. This pathway gave poor results due to low transesterification yield, as observed by ^{1}H NMR (<10%, even after 48 h in benzyl alcohol at 120 °C). Furthermore, the depolymerization step under high vacuum and temperature toward formation of cyanoacrylate benzyl ester resulted in poor yields and purity.

The synthesis described in Scheme 2 involves reaction of ethyl cyanoacrylate (**1**) with anthracene (**2**) to form a Diels–Alder adduct (**3**).where R is

The ester moiety of adduct **3** can be manipulated avoiding polymerization of **1**. The ethyl ester of the adduct was removed by basic hydrolysis under mild conditions to afford anthracene–cyanoacrylic acid adduct (**4**), which is then esterified with the desired alcohol to render the adduct ester (**5**). Monomeric cyanoacrylate esters were displaced from adduct **5** by retro-Diels–Alder with maleic anhydride.

Scheme 2. Synthesis of Cyanoacrylate Esters via Anthracene Adduct



Ethyl cyanoacrylate–anthracene adduct (**3**) was formed in high yield from the reaction of 1.5 molar excess cyanoacrylate to anthracene (**2**) in toluene. The hydrolysis of the ethyl ester proceeded smoothly at room temperature. Very pure anthracene-cyanoacrylic acid (**4**) was easily isolated at 90% yield. From all conventional esterification methods tested, the dicyclohexyl carbodiimide (DCC) coupling reagent in the presence of dimethyl aminopyridine (DMAP) in dichloromethane was most effective. Pure esters (**5**) were obtained in about 90% yield after crystallization. This reaction was scaled up to a 50 g scale. The last step in this synthesis was the retro-Diels–Alder reaction. The desired cyanoacrylate ester-anthracene adduct was refluxed in xylene in the presence of maleic anhydride. Maleic anhydride–anthracene adduct (**6**) crystallized from the reaction mixture on cooling with 98% recovery. Cyanoacrylate esters (**7**) were isolated by removal of the solvent under reduced pressure and/or crystallizations.

From the substances synthesized, only the dansyl ethanolamide (**5h**) derivative could not be isolated as a monomer, probably due to the protonation of the dimethyl amine moiety. A base is required to release the free base form, which rapidly polymerizes, impeding its isolation. ^{1}H NMR data of substances obtained in every step are provided in the Experimental Section.

3.2. Fingerprint Development. *3.2.1. Fume Development.* First development experiments were carried out with the new cyanoacrylate ester adducts with anthracene mixed with an excess of maleic anhydride.. The mixture was heated to 200 °C in a regular cyanoacrylate fuming chamber. Exhibits were observed under UV light after ventilating the chamber. Results show that the surfaces tested were coated with a substance having blue fluorescence, which could be easily removed. Fingermarks, however, were not developed. The liquid remaining in the heating recipient solidified quickly on cooling. Analysis of the remaining mixture showed the presence of the benzyl cyanoacrylate-anthracene adduct and maleic anhydride, together with other unknown substances. Expected maleic anhydride-anthracene adduct was not detected in the mixture. It is believed that some adduct underwent retro-Diels–Alder. The released anthracene rapidly sublimated before it could react with maleic anhydride, thus coating the exhibits without developing fingermarks.

Further experiments were conducted with the synthesized cyanoacrylates as pure materials and as mixtures with Superglue at atmospheric pressure. The experiments were performed in a fuming chamber heating up to 150 °C. Fumes did not evolve when pure materials were used. Fingermark development was not observed on the exhibits. Fingermark development was

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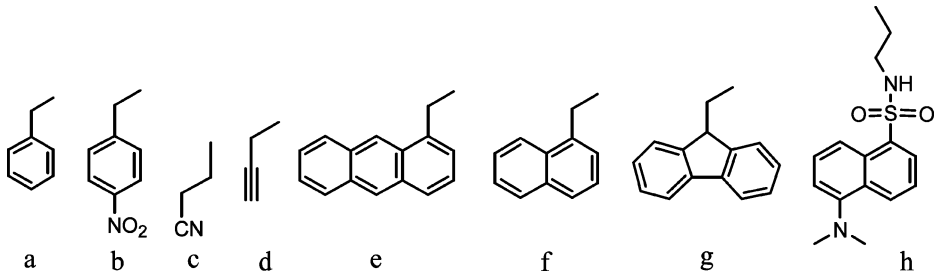
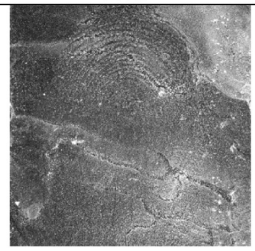
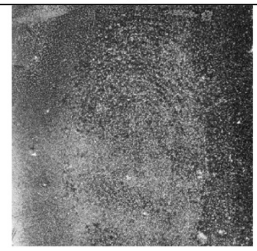
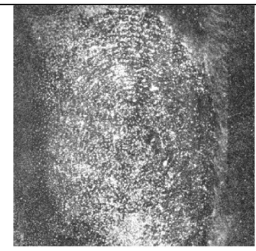
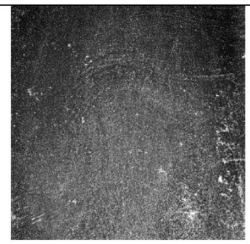
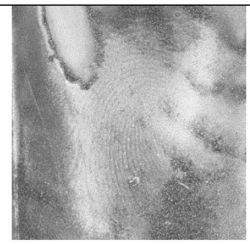
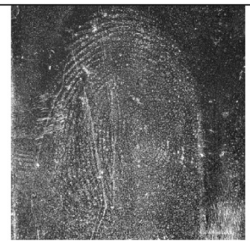
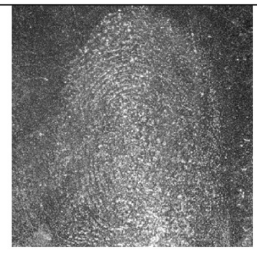
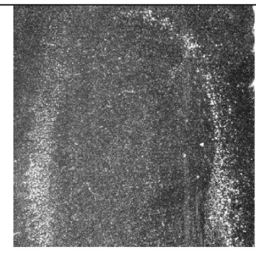


Table 1. Fingerprint Development in 1, 5, and 10% w/v Ethyl Cyanoacrylate Solutions in Dichloromethane, Ethyl Acetate, and Xylene

	1%	5%	10%
Dichloro methane			
Ethyl acetate			
Xylene			

observed with white light when the material was diluted with ethyl cyanoacrylate. No fluorescence, however, was observed by illumination of the exhibits under UV light, suggesting that only ethyl cyanoacrylate evaporated and developed the marks. New synthesized cyanoacrylate esters were not volatile enough at atmospheric pressure to afford fingermark development in a regular fuming chamber.

Experiments conducted in a vacuum rendered fixation of the fingermark as white ridges only when benzyl cyanoacrylate (**7a**), *p*-nitrobenzyl cyanoacrylate (**7b**), and anthracenemethyl cyanoacrylate (**7e**) were used as developing materials. Developed slides were observed under UV light (350 nm) and blue light (415−490 nm) using a polilight apparatus. In addition, slides were observed by fluorescence microscopy in the reflection mode. Slides developed by the benzyl ester did not react to illumination by either method.

Slides developed by *p*-nitrobenzyl (**7b**) and anthracene-methyl (**7e**) derivatives showed very weak fluorescence when observed with fluorescence microscopy. Moreover, the residues remaining in the heating boat after development revealed high intensity orange fluorescence under blue light for **7b** and yellow fluorescence under UV light for **7e**; monomers were also observed before heating. It is believed that only small amounts of the substance are polymerized on the fingermark.

3.2.2. Solution development. Because of these limitations and inspired by a development procedure suggested by Mr. Reiko Hiyoshi from a forensic unit in Japan, the authors tried fingermark development in solution. A series of solvents were examined as candidates for fingerprint solution development. Chlorinated hydrocarbons, aliphatic and aromatic hydrocarbons and ethers were examined. Xylene met two basic conditions; it dissolved cyanoacrylate esters without causing their instant polymerization, and fingerprints were not excessively damaged upon contact with the solvent. Regular ethyl cyanoacrylate (ECA) (**1**) was used to test the concept and to measure optimal concentration in solution. Glass slides with fingerprints were dipped for few seconds into the cyanoacrylate solution and left to dry in a hood at room temperature. Data for fingerprint development in dichloromethane, ethyl acetate, and

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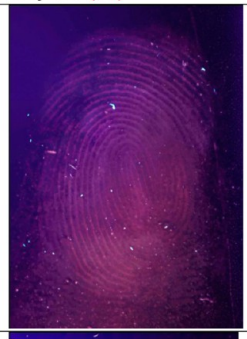
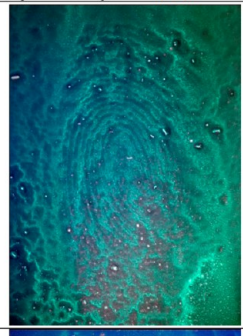
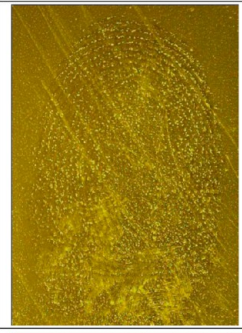
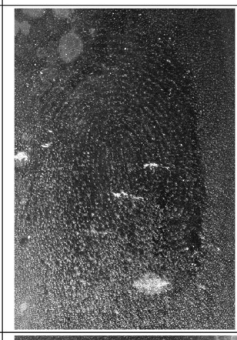
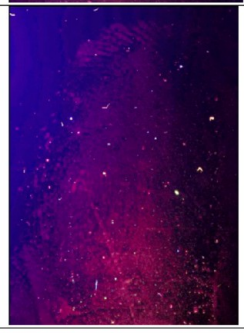
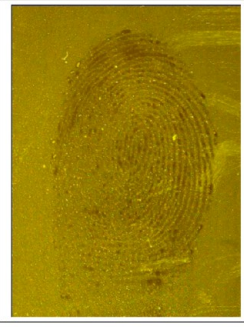
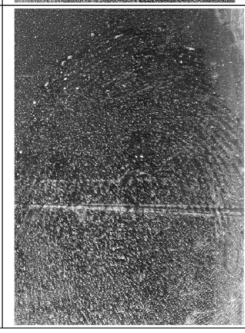
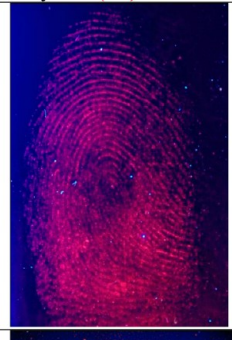
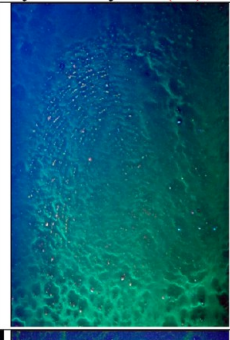
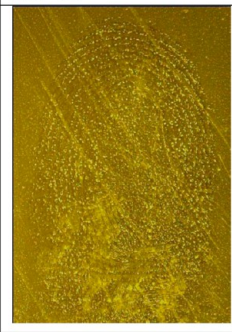
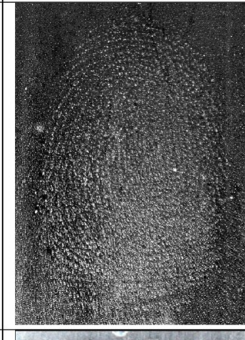
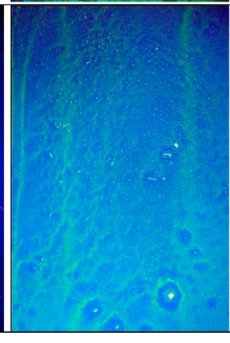
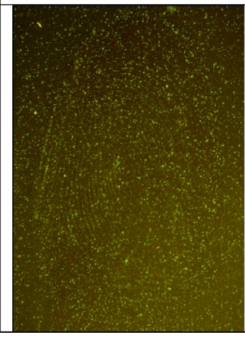
Table 2. (a) Development of Eccrinic Fingerprints Using 1% Cyanoacrylates in Xylene and (b) Development of Sebaceous Fingerprints Using 1% Cyanoacrylates in Xylene

a)

	p-nitrobenzyl cyano acrylate (7b)	Anthracenemethenyl cyanoacrylate (7c)	Ethyl cyanoacrylate+ BY-40	Ethyl cyanoacrylate
Eccrinic, 1 hr				
Eccrinic, 1 day				

b)

	p-nitrobenzyl cyano acrylate (7b)	Anthracenemethenyl cyano acrylate (7c)	Ethyl cyanoacrylate+ BY-40	Ethyl cyanoacrylate
Sebaceous, 1 hr				
Sebaceous, 1 day				

xylene at different ethyl cyanoacrylate concentration is given in Table 1.

Best results were obtained with 1% v/v ECA in xylene. Following this model, 1% solutions of nitrobenzyl (**7b**) and anthracenemethyl (**7e**) cyanoacrylates were prepared in xylene. As a reference, 1% solutions of ECA were also prepared, one of which containing the fluorescent dye basic yellow 40 (BY-40). Sebaceous and eccrine prints were deposited on microscope glass slides. Fresh and 1 day old prints were immersed in the cyanoacrylate solution for few seconds and dried in a hood. All of the marks developed on the slides were photographed under incident white light. In addition, fingerprints developed with the new cyanoacrylates were photographed under transmitted UV illumination (350 nm) using lenses equipped with a

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standard UV filter. Prints developed by BY-40 fluorescent dye and ECA containing solution were photographed under transmitted blue light (450 nm) and lenses equipped with an orange filter. Results are listed in Table 2, parts a and b.

Fingerprints developed with p-nitrobenzyl derivative (**7b**) were clearly visible except the 1 day old eccrinic print. They showed magenta fluorescence under 350 nm illumination. Development with the anthracenyl derivative (**7e**) afforded good quality prints when observed under white light. However, lesser quality was observed under UV light due to background fluoresce in yellow-greenish color. Development by ECA solutions gave more background around the prints, but reasonable good images were still observed under white light. The background problem is emphasized when ECA-BY-40 prints are observed under blue light. Sebaceous fingermarks elicited better results than eccrine fingermarks, perhaps due to the nature of the polymer produced. *p*-Nitrobenzyl derivative (**7b**) generated very good fluorescent results for the sebaceous fingermarks although less so for the one day old eccrine fingerprints. The antracenyl derivative (**7e**) afforded reasonable development of prints when observed under white light. Fluorescence observation, however, yielded poor resolved prints. Eccrine and sebaceous prints showed good development with ethyl cyanoacrylate + By-40, although the background fluoresced as well under blue illumination (450 nm). Among the substances tested, p-nitrobenzyl derivative (**7b**) succeeded in developing both sebaceous and eccrine prints. This substance produced high quality images under white light mode and under fluorescence mode.

4. CONCLUSIONS

New fluorescent cyanoacrylates have been synthesized at high yield and purity using anthracene adducts process. These monomers were found effective in fingerprint development by surface polymerization in solution. This synthetic method of ester exchange can be scaled-up where the protecting and deprotecting groups, anthracene and maleic anhydride are recyclable. These monomers may have applications in the design of new glue sealants and coatings.

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Notes

The authors declare no competing financial interest.

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