Chemical Modification of the Pendant Structure of Wholly Aromatic Polyamides: Toward Functional High-Performance Materials with Tuned Chromogenic and Fluorogenic Behavior

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ABSTRACT: This work describes the preparation of functional aromatic polyamides with pendant fluorescent chemical structures. The preparation of a parent copolyamide with a lateral fluorene moiety anchored to the main chain through a urea group is described, along with the chemical modification of the fluorene moieties to render six copolymers with different fluorescent behaviors. The easy and clean chemical modification of the polyamide structure permits the preparation of high-performance materials with "a la carte" fluorescence properties. The characteristics of these materials make them useful for cutting-edge technologies associated with the fluorescence of the pendant fluorene moiety and with the host behavior of the urea motif, that is, fluorescent sensing of analytes or hybrid luminescent converter—light-emitting diode systems. The chemical modification of the polymer structure was carried out with chemicals and conditions optimized for polyamide models. The influence of the chemical structure of the pendant fluorene core has also been addressed in terms of thermal properties, solubility, water uptake, and so forth. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3823–3833, 2010

KEYWORDS: binding sites; copolyamides; fluorescence or fluorescent; functionalization of polymers; luminescence; luminescent converter; LUCO; polyamides; signaling units

INTRODUCTION Chemical functionalization of the structure of high-performance materials, that is, aramids, expands their applicability to new and cutting-edge fields.¹ Thus, the inclusion of chromogenic and fluorescent chemical moieties in the lateral aromatic polyamide chains¹ can give rise to luminescent converter (LUCO) materials, which in combination with a primary pumping source, that is, blue light-emitting diodes (LEDs), permits the preparation of LEDs with tremendous potential in lighting and backlighting applications.¹⁻¹⁹ In addition, if the chromogenic and fluorescent moieties include a substructure capable of interacting selectively with analytes, the variations in the chromogenic or fluorescent behavior of the material permit the preparation of chemical sensors that could be used to detect analytes using the different spectral characteristics of light emitted by hybrid LUCO/LED devices or by fine tuning the visual perception of their emitted light (color). In parallel, if the functionalization gives rise to colored host substructures, the interaction with guest analytes may also lead to color changes, which could give rise to "naked eye" colorimetric sensing materials.²⁰⁻²⁴

The design and preparation of organic functional materials can be carried out by two methods: by synthesis of monomers containing the desired functionality or by modification of the chemical structure of a parent polymer. The latter has advantages related to the economics of the process, and it opens a way for total or partial modification of the parent structure with the desired functionality while still retaining the properties of the parental compound to a degree, including the characteristics of the functional groups.

Chemical modification of high-performance materials, especially of aromatic polyamides, is rarely performed. Few successful examples have been published in the literature due to their insolubility and to the presence of amide linkages that can undergo side reactions.

Herein, we describe the preparation of novel aromatic polyamides with pendant structures comprised of a fluorene-substituted urea group, where the urea group is an excellent binding site and the fluorene acts as a signaling unit due to its fluorescent and sometime chromogenic characteristics. We previously succeeded in the use of these functional groups to prepare polymers with specialty properties.^{17,25–28} The fluorene moiety was chemically modified to alter its fluorescent behavior by introducing the following groups: carbonyl, hydroxy, oxime, hydrazone, and dicyanomethylene. The chemical modification of a parent polyamide permits the preparation of a series of polymers presenting different

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properties, such as fluorescent behavior, binding characteristics, and reactive functional groups.

We prepared and analyzed a chemically modified copolyamide consisting of 90% of structural units of poly(*m*-phenylene isophthalamide) (NOMEX[®]) and 10% of structural units containing the pendant fluorene groups. We used the copolymer to maintain the outstanding mechanical and thermal properties of NOMEX[®] to give rise to creasable films or dense membranes to be used as colorimetric or fluorescence sensing materials.¹ Moreover, a 10% mole content of the structural units with the urea binding site and fluorescent fluorene group is adequate for measuring changes in the fluorescence behavior upon interaction with analytes and sufficient for giving rise to perceptible "naked eye" colorimetric variations.

The ease and effectiveness of the polymer modification reactions have been carried out following orthogonal and high yielding reactions and were previously studied using model compounds. This synthetic approach has proven to be a rally adequate strategy to prepare new functional soft materials.²⁹ The models chemically resemble the polymers, and their low molecular weight permits studying the reactions in terms of cleanliness, conversion, and yield using conventional purification and characterization techniques. The reaction conditions were optimized with the model compounds and then applied to the polymers. These model compounds were also used to study the chromogenic and fluorogenic behavior of the polymers in solution, supposing that each model mimics the behavior of its corresponding polymer, but with a defined molecular weight and higher solubility.^{30,31}

EXPERIMENTAL

All materials and solvents were obtained commercially and used as received unless otherwise indicated. *N*-Methyl-2-pyrrolidone (NMP; Aldrich) was vacuum distilled twice over phosphorus pentoxide and then stored over 4-Å molecular sieves. Lithium chloride (Aldrich) was dried at 400 °C for 12 h before use. Triphenylphosphite (TPP; Aldrich) was vacuum distilled twice over calcium hydride and then stored over 4-Å molecular sieves. Pyridine (Merck) was dried by refluxing over sodium hydroxide for 24 h and then distilled over 4-Å molecular sieves. *m*-Phenylenediamine (MPD) was purchased from Aldrich and purified by double vacuum sub-limation. Isophthalic acid (IA) was purified by crystallization (3 g in 1.2 L of boiling water). 9*H*-Fluoren-2-yl isocyanate (Aldrich, 98%) was used as received.

MONOMER AND MODELS

5-[3-(9H-Fluoren-2-yl)ureido]isophthalic Diethyl Ester (1)

5-Amino diethyl isophthalate (5 g, 24 mmol) was dissolved in 100 mL of *N*,*N*-dimethylacetamide containing 3.70 mL (29 mmol) of trimethylchlorosilane in a 250-mL round-bottomed flask fit with a magnetic stirrer. Then, 9*H*-fluoren-2-yl isocyanate (24 mmol) was added portionwise and the resulting solution was stirred at room temperature for 24 h and then precipitated in 500 mL of slightly acidified water. The product (1) was filtered off, washed thoroughly with distilled water, and dried in a vacuum oven at 80 $^{\circ}$ C overnight. Yield: 95%. M.p.: 276 $^{\circ}$ C (dec.).

¹H-NMR (400 MHz, [*D*₆]DMSO, *δ*, ppm): 9.31 (s, 1H, NH); 8.84 (s, 1H, NH); 8.36 (s, 2H, Ph); 8.10 (s, 1H, Ph); 7.83 (m, 3H, Ph); 7.57 (d, 1H, *J* = 7.2 Hz, Ph); 7.45 (d, 1H, *J* = 8.1 Hz, Ph); 7.38 (t, 1H, *J* = 7.2 Hz, Ph); 7.28 (t, 1H, *J* = 7.5 Hz, Ph); 4.4 (q, 4H, *J* = 6.9 Hz, *CH*₂CH₃); 3.93 (s, 2H, Fluorene); 1.38 (t, 6H, *J* = 6.9 Hz, CH₂CH₃). ¹³C NMR (100.6 MHz, [*D*₆]DMSO: *δ*, ppm); 165.68; 153.54; 154.00; 143.64; 142.04; 141.76; 139.28; 136.51; 132.00; 127.63; 126.82; 126.00; 123.50; 123.45; 120.48; 118.39; 116.35; 82.16; 37.40; 15.10. FTIR (cm⁻¹): v_{N-H} : 3300; δ_{N-H} : 1614; v_{Ar} _{C=C}: 1563; $v_{C=O}$: 1750;1730.

5-[3-(9H-Fluoren-2-yl)ureido]isophthalic Acid (2)

5-[3-(9H-Fluoren-2-yl)ureido]isophthalic diethyl ester (10.50 g, 24 mmol) was mixed with 70 mL of NaOH (10%) and 100 mL of *N*,*N*-dimethylacetamide in a 100-mL round-bottomed flask fit with a magnetic stirrer. The resulting solution was stirred at 70 °C for 24 h and then precipitated in 500 mL of slightly acidified water. The product (**2**) was filtered off, washed thoroughly with distilled water, and dried in a vacuum oven at 80 °C overnight. Yield: 92%. M.p.: 299 °C (dec.).

¹H NMR (400 MHz, [*D*₆]DMSO, *δ*, ppm): 13.23 (s, 2H, CO₂H); 9.27 (s, 1H, NH); 8.93 (s, 1H, NH); 8.38 (s, 2H, Ph); 8.15 (s, 1H, Ph); 7.86 (m, 3H, *J* = 8.0 Hz, Ph); 7.58 (d, 1H, *J* = 7.6 Hz, Ph); 7.50 (d, 1H, *J* = 8.0 Hz. Ph), 7.36 (t, 1H, *J* = 7.2 Hz, Ph); 7.26 (t, 1H, *J* = 7.2 Hz, Ph), 3.93 (s, 2H, Fluorene). ¹³C NMR (100.6 MHz, [*D*₆]DMSO, *δ*, ppm): 167.73; 153.59; 144.93; 143.60; 142.12; 141.57; 139.52; 136.42; 132.83; 127.69; 126.85; 125.96; 124.23; 123.63; 121.19; 120.26; 118.40; 116.36; 37.52. FTIR (cm⁻¹): v_{N-H} : 3280; v_{O-H} : 3400 – 2750; $v_{C=0}$: 1716; 1640; δ_{N-H} : 1610; v_{Ar} C=C: 1558.

5-(3-9H-Fluoren-2-ylureido)-*N*,*N*[′]-diphenylisophthalamide (*M*1)

Aniline (2 mL, 30 mmol), diacid (2) (3 g, 7.7 mmol), and lithium chloride (1.08 g) were dissolved in a mixture of pyridine (4.6 mL), TPP (4.87 mL, 18.5 mmol), and NMP (15.5 mL) in a 50-mL three-necked flask fit with a mechanical stirrer. The resulting solution was stirred and heated at 110 °C under dry nitrogen for 4 h. The system was then cooled to room temperature and the solution was precipitated in 300 mL of methanol. The product obtained was filtered off, washed with methanol, extracted with acetone for 24 h in a Soxhlet apparatus and dried in a vacuum oven at 80 °C overnight. Yield: 72%. M.p.: 268 °C (dec.).

¹H NMR (400 MHz, [*D*₆]DMSO, *δ*, ppm): 10.47 (s, 2H, CONH); 9.20 (s, 1H, NH); 8.94 (s, 1H, NH); 8.26 (s, 2H, Ph); 8.18(s, 1H, Ph); 7.86(m, 7H, Ph); 7.60 (d, 1H, *J* = 7.2 Hz, Ph); 7.51 (d, 1H, *J* = 8.4Hz, Ph); 7.44 (m, 5H, Ph); 7.29 (t, 1H, *J* = 7.2 Hz, Ph); 7.17 (t, 2H, *J* = 7.2 Hz, Ph); 3.96 (s, 2H,). ¹³C NMR (100.6 MHz, [*D*₆]DMSO, *δ*, ppm): 166.16; 153.49; 144.89; 143.62; 142.04; 141.23; 141.03; 140.00; 139.45; 136.85; 129.70; 129.60; 127.74; 127.63; 126.57; 126.39; 124.82; 121.25; 120.80; 120.20; 118.25; 116.22; 37.45. FTIR (cm⁻¹): v_{N-H} : 3284; $v_{C=0}$: 1692 - 1646; δ_{N-H} : 1607; v_{Ar} C=C: 1561. Elemental analysis for $C_{34}H_{26}N_4O_3$ (538.31): calc (%) C 75.82, H 4.87, N 10.40; found (%) C 76.20, H 4.92, N 9.79.

5-(3-(9-0xo-9H-fluoren-2-yl)ureido)-N,N'diphenylisophthalamide (M2)

5-(3-9H-Fluoren-2-ylureido)-N,N'-diphenylisophthalamide (M1) (1.95 g, 3.62 mmol) was dissolved in 20 mL of dimethyl sulfoxide and cesium carbonate (3.54 g, 10.86 mmol) in a 100-mL round-bottomed flask. The resulting solution was stirred at room temperature for 6 days and then precipitated in 100 mL of water. The product (M2) was filtered off, washed thoroughly with distilled water, and dried in a vacuum oven at 60 °C overnight. Yield: 92.5%. M.p.: 226 °C (dec.).

¹H NMR (400 MHz, $[D_6]$ DMSO, δ , ppm): 10.48 (s, 2H, CONH); 9.30 (s, 1H, NH); 9.18 (s, 1H, NH); 8.26 (s, 2H, Ph); 8.21(s,1H, Ph); 7.92 (s, 1H, Ph); 7.87 (d, 4H, J = 8.0 Hz, Ph); 7.74 (d, 2H, J = 7.2 Hz, Ph); 7.63 (m, 3H, Ph); 7.44 (t, 4H, J = 7.6 Hz, Ph); 7.34 (t, 1H, J = 7.2 Hz, Ph); 7.18 (t, 2H, J = 7.2 Hz, Ph). ¹³C NMR (100.6 MHz, $[D_6]$ DMSO, δ , ppm): 194.08; 166.20; 153.53; 145.37; 145.22; 141.87; 141.07; 140.03; 138.28; 136.96; 136.31; 135.20; 134.38; 129.64; 129.30; 129.64; 124.80; 124.82; 122.62; 121.59; 121.33; 121.17; 115.10. FTIR (cm⁻¹): v_{N-H} : 3280; $v_{C=0}$: 1704–1649; δ_{N-H} : 1597; v_{Ar} _{C=C}: 1553. Elemental analysis for C34H24N4O4 (552.59): calc. (%) C 73.90, H 4.38, N 10.14; found (%) C 73.62, H 4.53, N 9.72.

5-(3-(9-Hydroxy-9H-fluoren-2-yl)ureido)-N,N'diphenylisophthalamide (M3)

5-(3-(9-Oxo-9H-fluoren-2-yl)ureido)-*N*,*N*'-diphenylisophthalamide (M2) (1.0 g, 1.8 mmol) was dissolved in 10 mL of N,Ndimethylacetamide and 0.13 g (3.36 mmol) of sodium borohydride in a 25-mL round-bottomed flask fit with a magnetic stirrer. The resulting solution was stirred at room temperature for 24 h and then precipitated in 100 mL of slightly acidified water. The product (M3) was filtered off, washed thoroughly with distilled water, and dried in a vacuum oven at 60 °C overnight. Yield: 93%. M.p.: 272 °C (dec.).

¹H NMR (400 MHz, [D_6]DMSO, δ , ppm): 10.46 (s, 2H, CONH); 9.20 (s, 1H, NH); 8.98 (s, 1H, NH); 8.25 (s, 2H, Ph); 8.17(s, 1H, Ph); 7.88(s, 1H, Ph), 7.85 (d, 4H, J = 8.0 Hz, Ph); 7.74 (m, 1H, Ph); 7.59 (d, 1H, J = 7.6 Hz, Ph); 7.50(d, 1H, J = 9.2 Hz, Ph); 7.42 (m, 6H, Ph); 7.28 (t, 1H, J = 7.2 Hz, Ph); 7.16 (t, 1H, J = 7.2 Hz, Ph), 5.89(d, 1H, J = 7.2 Hz, OH), 5.50 (d, 1H, J = 7.2 Hz, CH).¹³C NMR (100.6 MHz, [D_6]DMSO, δ , ppm): 166.15; 153.45; 148.89; 147.57; 141.06; 140.41; 140.00; 136.90; 135.76; 135.14; 134.42; 129.60; 129.50; 129.45; 127.39; 125.83; 124.73; 124.70; 121.25; 120.24; 119.34; 116.31; 74.53. FTIR (cm⁻¹): v_{N-H} : 3310; $v_{C=0}$: 1700–1630; δ_{N-H} : 1597; v_{Ar} _{C=C}: 1620–1680; v_{O-H} : 3200– 2450. Elemental analysis for C₃₄H₂₆N₄O₄ (554.60): calc (%) C 73.63, H 4.73, N 10.10; found (%) C 74.01, H 4.75, N 9.81.

g (1.0 mmol) of M2 was dissolved in 4 mL of N,N-dimethyl-

N, N'-diphenylisophthalamide(M4)

formamide and 0.14 g (2 mmol) of malononitrile. The resulting solution was stirred at 100 °C for 6 days and then precipitated in 100 mL of water. The product was filtered off, washed thoroughly with distilled water, extracted with acetone for 24 h in a Soxhlet apparatus and then dried in a vacuum oven at 60 °C overnight. Yield: 85.71%. M.p.: 297 °C (dec.).

In a 25-mL Erlenmeyer flask fit with a magnetic stirrer, 0.50

5-(3-(9-(Dicvanomethylene)-9H-fluoren-2-yl)ureido)-

¹H NMR (400 MHz, [D_6]DMSO, δ , ppm): 10.44 (s,2H, CONH); 9.16 (s,1H, NH); 9.15 (s,1H, NH); 8.21 (s,2H, Ph); 8.18 (s,1H, Ph); 8.13 (s,1H, Ph); 8.01 (d,1H, J = 7.6 Hz, Ph); 7.85 (d,4H, J = 8.0 Hz, Ph); 7.78 (m,1H, Ph); 7.57 (m,2H, Ph); 7.49 (t,1H, J = 8.0 Hz, Ph), 7.43 (t,4H, J = 7.6 Hz, Ph); 7.28 (t,1H, J =7.6 Hz. Ph); 7.18 (t,2H, I = 7.2 Hz, Ph). ¹³C NMR (100.6 MHz, [*D*₆]DMSO, δ, ppm): 166.18; 161.20; 153.50; 143.14; 141.50; 140.80; 140.00; 136.90; 136.20; 136.06; 136.00; 134.23; 129.60; 129.10; 126.70; 124.80; 124.60; 122.70; 121.36; 120.90; 116.90; 114.40; 114.10; 76.20. FTIR (cm⁻¹): v_{N-H} : 3290; $v_{C=N}$: 2213, $v_{C=0}$: 1680–1646; δ_{N-H} : 1610; v_{Ar} $_{C=C}$: 1547. Elemental analysis for $C_{37}H_{24}N_6O_3$ (600.64): calc (%) C 73.99, H 4.03, N 13.99; found (%) C 73.68, H 4.12, N 13.54.

(5-(3-(9-(Hydroxyimine)-9H-fluoren-2-yl)ureido)-N,N'diphenylisophthalamide (M5)

In a 25-mL Erlenmeyer flask fit with a magnetic stirrer, 0.50 g (1.0 mmol) of M2 was dissolved in 5 mL of N,N-dimethylformamide and 0.076 g (1.1 mmol) of hydroxylamine hydrochloride. The resulting solution was stirred at 80 $^\circ$ C for 24 h and then precipitated in 15 mL of water. The product (M5), an equimolecular mixture of Z and E isomers, was filtered off, washed thoroughly with distilled water, extracted with acetone for 24 h in a Soxhlet apparatus and then dried in a vacuum oven at 60 °C overnight. Yield: 76%. M.p.: 270 °C (dec.).

¹H NMR (400 MHz, $[D_6]$ DMSO, δ , ppm): 12.60 (s, 1H, OH); 12.55 (s, 1H, OH); 10.48 (s, 2H, CONH,); 9.22 (s, 1H, NH); 9.15 (S, 1H, NH); 9.12 (S, 1H, NH), 9.06 (S, 1H, NH), 8.61 (d, 1H, I = 7.2 Hz, Ph); 8.35 (d, 1H, I = 7.2 Hz, Ph); 8.26 (s, 2H, Ph), 8.2 (s, 1H, Ph); 7.85 (m, 6H, Ph), 7.44 (m, 7H, Ph); 7.18 (t, 2H, J = 7.2 Hz, Ph). 12.55 (s, 1H, OH); 10.48 (s, 2H, CONH,); 9.12 (s, 1H, NH); 9.06 (S, 1H, NH); 8.26 (s, 2H, Ph), 8.20 (s, 1H, Ph); 8.02 (d, 1H, J 7.2 Hz, Ph); 7.85 (m, 6H, Ph), 7.72(d, 1H, J 7.2 Hz, Ph), 7.44(m, 7H, Ph); 7.18 (t, 2H, J 7.2 Hz, Ph).¹³C NMR (100.6 MHz, [D_6]DMSO, δ, ppm): 166.18; 153.51; 152.08; 141.38; 141.01; 140.71; 140.52; 140.00; 137.26; 136.94; 136.14; 135.22; 134.43; 131.73; 131.34; 129.63; 128.34; 124.74; 121.30; 121.07; 120.57; 120.05; 111.29. FTIR (cm⁻¹): v_{N-H} : 3340; $v_{C=0}$: 1710–1625; δ_{N-H} : 1605; *v*_{Ar C=C}: 1610–1685; *v*_{O-H}: 3210–2510. Elemental analysis for C34H25N5O4 (567.60): calc (%) C 71.95, H 4.44, N 12.34; found (%) C 72.13, H 4.73, N 11.96.



SCHEME 1 Experimental monomer and model synthesis (M5 and M6 were obtained as equimolecular mixtures of Z and E isomers).

5-(3-(9-Hydrazone-9H-fluoren-2-yl)ureido)-*N,N'*diphenylisophthalamide (M6)

In a 25-mL Erlenmeyer flask fit with a magnetic stirrer, 0.50 g (1.0 mmol) of **M2** was dissolved in 5 mL of *N*,*N*-dimethylformamide and 1 mL (20 mmol) of hydrazine monohydrate. The resulting solution was stirred at room temperature for 48 h and then precipitated in 15 mL of methanol. The product (**M6**), an equimolecular mixture of Z and E isomers, was filtered off, washed thoroughly with distilled water, extracted with acetone for 24 h in a Soxhlet apparatus and then dried in a vacuum oven at 60 °C overnight. Yield: 71%. M.p.: 275 °C (dec.).

¹H NMR (400 MHz, [D_6]DMSO, δ , ppm): 10.52 (s, 2H, CONH); 9.25 (s, 1H, NH); 9.03 (s, 1H, NH); 8.30 (s, 2H, Ph); 8.22(s, 1H, Ph); 7.85(m, 7H, Ph); 7.62 (d, 1H, J = 7.2 Hz); 7.41 (m, 7H, Ph); 7.30 (t, 2H, J = 7.2 Hz, Ph); 5.95(d, 1H, J = 7.2 Hz, NH₂); 5.53(d, 1H J = 7.2 Hz, NH₂).¹³C NMR (100.6 MHz, $[D_6]$ DMSO, δ , ppm): 166.27; 163.30, 153.56; 149.01; 147.61;141.19; 140.52; 140.10; 137.00; 135.76; 134.52; 134.42; 129.70; 129.60; 127.49; 125.95; 124.83; 121.34; 121.27; 120.21; 119.43; 119.40; 116.18. FTIR (cm⁻¹): ν_{N-H} : 3310; $\nu_{C=0}$: 1700–1630; δ_{N-H} : 1597; $\nu_{ArC=C}$: 1620–1680; ν_{O-H} : 3200–2450. Elemental analysis for C₃₄H₂₆N₆O₃ (566.62): calc (%) C 72.07, H 4.63, N 14.83; found (%) C 71.70, H 4.67, N14.44.

The overall monomer and model synthesis is shown in Scheme 1.



SCHEME 2 Synthesis and chemical structure of polyamide CP1.

Copolymer Synthesis

The copolymerization of the diacid (2) to give the copolymer **CP** (Scheme 2) was carried out as follows: MPD (20 mmol), diacid (2) (2 mmol), IA (18 mmol), and lithium chloride (2.8 g) were dissolved in a mixture of pyridine (12 mL), TPP (44 mmol), and NMP (40 mL) in a 200-mL three-necked flask fit with a mechanical stirrer, and the resulting solution was stirred and heated at 110 °C under dry nitrogen for 4 h. The system was then cooled to room temperature and the solution was precipitated in 300 mL of methanol to give a swollen fibrous precipitate. The obtained copolymer was filtered off, washed with distilled water and acetone, extracted with acetone for 24 h in a Soxhlet apparatus, and finally dried in a vacuum oven at 80 °C overnight. The yield was quantitative.

Chemical modification of the copolymer **CP1** to yield the modified copolymers (**CP2-6**) was carried out following the procedures described in the preparation of the models **M2-6** from model **M1**.

The copolymer synthesis and acronyms are depicted in Schemes 2 and 3.

MEASUREMENTS AND INSTRUMENTATION

¹H and ¹³C NMR spectra were recorded with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively, using deuterated dimethylsulfoxide ($[D_6]$ DMSO) as solvent. Low-resolution electron impact (EI-LR) mass spectra were obtained at 70 eV on an Agilent 6890N mass spectrometer. High-resolution mass spectrometry (HRMS) was carried out on a Micromass AutoSpect Waters mass spectrometer. Infrared spectra (FTIR) were recorded with a Nicolet Impact spectrometer. Elemental analyses were performed with a LECO CHNS-932 microanalyzer. Inherent viscosities were measured with an Ubbelohde viscometer at 25 \pm 0.1 °C with NMP as the solvent at a concentration of 0.5 g/dL. UV/Vis and fluorescence spectra were recorded on a Varian Cary3-Bio UV-Vis spectrophotometer and a Varian Cary Eclipse fluorometer, respectively. Thermogravimetric analysis (TGA) data were recorded on 5 mg of sample under nitrogen or oxygen with a TA Instruments Q50 TGA analyzer at a scan rate of 10 °C/min. Polymer solubility was determined by mixing 10 mg of sample with 1 mL of solvent and then stirring for 24 h at room temperature. Polymer films were prepared by evaporation of cast solutions in NMP. In most cases, a concentration of 10% by polymer weight was used and the solvent was eliminated by heating at 100 °C for 4 h in an air-circulating oven and then at 120 °C for 4 h under vacuum (1 mm Hg). Water sorption values were determined gravimetrically at room temperature. Powdered polymeric samples of about 200 mg, previously dried at 120 °C for 24 h over phosphorus pentoxide, were placed in a closed box containing a saturated aqueous solution of NaNO₂ at a temperature of 20 °C, which provided a relative humidity of 65%. The samples were weighed periodically over 8 days until they equilibrated with their surroundings and presented no further changes in weight.

RESULTS AND DISCUSSION

Our work concerns the design, preparation, and characterization of high-performance functional materials for future use



SCHEME 3 Chemical structure and codes of the modified copolyamides.



FIGURE 1 Characterization of model M2 by (a) FTIR, (b) ¹H NMR, and (c) ¹³C NMR.

in advanced applications, especially in molecular recognition and in light-emitting hybrid LUCO/LED systems. Therefore, we describe copoly(isophthalamide)s containing urea binding sites in the polyamide backbone along with a substituted fluorene motif as the fluorescent signaling subunit (Scheme 2). The copolymers with different fluorene moieties were derived from a parent copolymer containing the unmodified fluorene group (Scheme 3).

Chemical modifications of the pendant copolymer structure were carried out following easy and clean reactions. The introduction of new chemical functions in position 9 of the fluorene ring clearly modifies the overall electron density over the fluorene and the urea group. This modification permits the tuning of: (a) the fluorescence and the signaling behavior of the group; and (b) the receptor capability of the urea motif. Moreover, the introduced functional groups permit further reactivity on the polymer, thereby opening new possibilities in terms of the applicability of the Nomex-like aromatic polyamides.

Monomer, Polyamide Models, and Polymer Synthesis and Characterization

The diacid monomer **2** was previously prepared in an easy clean way by reaction of 2-isocyanato-9H-fluorene with 5-aminoisophthalic acid to produce a diacid monomer containing the urea binding site and a fluorene motif in high yield and purity.

The reaction of the diacid monomer **2** with 2 eq of aniline using high-temperature polymerization conditions, the so-called Yamazaki method,³² yielded model **M1** (Scheme 1) in a quantitative manner. The oxidation of the model with ce-sium carbonate/air transformed the fluorene group into fluorenone. The carbonyl group of fluorenone could be reduced



FIGURE 2 ¹H NMR spectrum of copolyamide CP1 and CP3.

to an alcohol (racemic mixture) and reacted with malononitrile to give the dicyanomethylene derivative; or with hydrazine to yield the hydrazone; or with hydroxylamine to give the oxime. The oxime and hydrazone were obtained as equimolecular mixtures of the Z and E isomers. Moreover, monomers **M5** and **M6** could be transformed again into **M1** by a simple hydrogenation step using Pd/C as catalyst. The models were purified by extraction with acetone for 24 h in a Soxhlet apparatus.

The intermediates, monomer, and models were characterized by IR and 1 H- and 13 C NMR spectroscopy, fully confirming the chemical structure of all of the products. As an illustrative example, Figure 1 depicts the chemical characterization of **M2**.

The copolyamide CP1 was synthesized by combining isophthalic acid (0.9 eq), diacid 2 (0.1 eq), and MPD (1 eq) following the Yamazaki method (Scheme 2).32 Every reaction with the model compounds was optimized to give higher yield and purity so that these conditions could be applied to the modification of the copolymer. Similar conditions were used to modify the pendant fluorene structure of copolymer CP1 to give copolymers CP2-6. Figure 2 shows the chemical characterization of copolymers CP1 and CP3 as an example. The peaks of the ¹H spectrum were assigned based on spectra of the model and were consistent with a quantitative modification of the pendant fluorene moiety. The NMR spectra showed a complete conversion of the parent polyamide (CP1) to copolymers CP2-CP6. This was analyzed by means of the disappearance of the ¹H signal in position 9 of the fluorene ring (see Fig. 2). Nevertheless, the lower molar content of the diacid residue containing the fluorene motif (10%) in conjunction with the low sensitivity of the NMR technique permits to assure that the conversion was significantly high, and it is not possible to guarantee a quantitative conversion.

The inherent viscosity of the parent copolymer **CP1** is 0.87 dL/g, which is significantly higher than 0.5 dL/g and indicates the formation of a high molecular weight copolymer. In addition, the creasable films obtained from this polymer upon casting are also suggestive of copolymer formation. Chemical modification of the pendant fluorene group of **CP1** to produce the other copolymers, **CP2-CP6**, influences the inherent viscosity. Changes in viscosity lead to different hydrodynamic volumes in solution of polymers with the same average polymerization degree (see Table 1 for η_{inh} data).

POLYMER PROPERTIES

Thermal Properties

The thermal behavior of the copolyamides was evaluated by TGA, and the results are shown in Table 1. The decomposition temperatures (T_d) of all polymers range between 254 and 332 °C (Table 1). This degradation step corresponds with a weight loss lower than 10% and accounts for the loss of the lateral chain, thus giving rise to a nomex-like structure, which is responsible for the second degradation step around 400 °C. In regards to the first degradation processes, different authors have described the oxidative degradation of urea units to occur at temperatures between 250 and 300 °C in urea-formaldehyde resins.^{33,34} The derivative curves of the TGA data show a different thermal behavior of the copolymers in oxidizing and inert atmospheres (see Fig. 3).

In regards to the char residue at 700 °C, the copolymers had values higher than 50%, corresponding to heat-resistant polymers. The char yield can be use to estimate the limiting oxygen index (LOI) of the polymers using the experimental Van Krevelen equation (LOI = 17.5 + 0.4 CR, where CR is the char yield in % weight).³⁵ The polymers had LOI values higher than 36, meaning that the polymer can be classified

		TGAª				
		N ₂ Atmosphere		O ₂ Atmosphere ^b		
Polymer	$\eta_{ m inh}$ (dL g $^{-1}$)	<i>T</i> _d (°C)	Char yield (%)	<i>T</i> _d (°C)	LOI	
CP1	0.87	265	58	265	40.7	
CP2	0.60	265	51	260	37.9	
CP3	0.74	255	59	260	41.1	
CP4	0.97	280	58	280	40.7	
CP5	0.75	255	60	255	41.5	
CP6	0.70	260	47	260	36.3	

 a T_d is the initial temperature at the onset of the first stage of the thermal weight loss. Char yield at 700 $^\circ\text{C}.$

^b The weight loss at 700 °C under oxygen is complete.



FIGURE 3 TGA curves of polyamide **CP2** under N_2 and O_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

as self-extinguishing polymers (LOI is defined as the minimum fraction of oxygen in a mixture of oxygen and nitrogen that will just support combustion after ignition. As air contains \sim 21% oxygen, any material with a LOI lower than 21 will probably hold up burning in an open-air situation).

Solubility and Water Sorption

The copolymer solubilities are shown in Table 2. The solubilities of the aromatic polyamides are high and comparable to that of the nomex. Therefore, these copolymers can be easily transformed upon solution by "casting" and we prepared creasable films in NMP solutions of the copolymers.

Aromatic polyamides are hydrophilic polymers due to their polar amide groups, whose interactions with water lead to water uptake from the environment. These water molecules interact with amide groups by weakening the amide–amide interactions that give the polyamides their high cohesive energy and consequently their high thermal transitions and resistance and superior mechanical properties. Therefore, the water uptake determines the final application of these high-performance materials as the absorbed water diminishes the $T_{\rm g}$ and influences the mechanical, electrical, and dielectric properties. Conversely, in other technological fields, such as membrane technology, greater water uptake in

TABLE 2 Solubility^a and Water Sorption of the Copolyamides

	NMP, DMA, DMSO	DMF	<i>m</i> -Cresol	Water Uptake (%)
CP1	++	++	+	8.4
CP2	++	++	+-	9.2
CP3	++	++	+	8.8
CP4	++	++	_	8.3
CP5	++	++	+-	8.7
CP6	++	++	+	9.4

a ++ = soluble at room temperature; + = soluble on heating; + = partially soluble; - = insoluble.



FIGURE 4 Solution of models **M1**, **M2**, **M3**, **M4**, **M5**, and **M6** (from left to right) in NMP (10^{-3} M): (a) upper photograph: without added anion; (b) lower photograph: with a fluoride concentration of 5 × 10^{-3} M (fluoride added as [CH₃ (CH₂)₃]₄NF). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water-treatment membranes or even in dense gas-separation membranes is generally associated with better performance.

The copolyamides described herein have a nomex-like structure with two amide groups per structural unit and a polar pendant structure in 10% of the diacid residue. The polarity



FIGURE 5 Fluorescence emission of a film (red line) and a DMSO solution (blue line) of polyamide **CP1** along with a fluorescence image of the polyamide (right: film obtained by casting; left: 4×10^{-3} M solution in DMSO). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]



FIGURE 6 Fluorescence image of copolyamides in solutions in solid state (films). From left to right: **CP1**, **CP2**, **CP3**, **CP4**, **CP5**, and **CP6**. The polymer concentration in solution of DMSO was 4×10^{-3} M (equivalents of fluorene residue/L). The photograph was taken under irradiation with UV (365 nm).

of the pendant chain depends mainly on the highly polar urea group and in the chemical functionalization of carbon 9 within the fluorene residue. Measurement of the isothermal sorption of water at 65% relative humidity gave values in accordance with the polyamide chemical structure (Table 2). The water uptake is high for fully aromatic polyamides and depends on the functionalization of the fluorene moieties. Thus, the presence of hydroxyl groups (**CP3** and **CP5**) or amine groups (**CP6**) increases the hydrophilic character of the materials, thus increasing the water uptake.

Chromogenic and Fluorescence Behavior

As previously outlined, the chromogenic and fluorescent behaviors of high-performance polymers are key properties for many novel applications, such as for chromogenic and fluorogenic sensing materials or for hybrid LUCO/LED emitting devices.

The colors of the model compounds in solutions and of the copolymers, both in solution and in the solid state, range from colorless to brown or yellow. The completely colorless solutions correspond to the model and copolymer containing the unmodified fluorene moiety (**M1** and **CP1**, respectively). The functionalization of the sp³ carbon (C9) of the fluorene gives rise to a color development in solution because of the intramolecular charge transfer (ICT) between the feeble electron-donating urea groups³⁶ and the chemical functions that

 TABLE 3
 Fluorescence Emission Maxima (nm) of Copolymers and Models

Polymer	Solution ^a	Solid State (film)	Model	Solution ^b
CP1	424	460	M1	425, 460 ^c
CP2	569, 594 ^c	577	M2	569, <mark>594</mark> °
CP3	420	422	M3	420
CP4	569, 600 ^c	<u>575</u> , 598	M4	530, <u>570</u> °
CP5	521	528	M5	517
CP6	432	447, 514	M6	467

 a 4 \times 10 $^{-3}$ M solution in DMSO.

 $^{\rm b}$ 2 \times 10 $^{-3}$ M solution in DMSO.

^c A maximum (underlined) and a shoulder were observed.

have an electron-withdrawing behavior (mainly in models and copolymers **M1**, **M2**, **CP1**, and **CP2**). The color of the model can be somewhat correlated with the HOMO-LUMO gap,³⁷ being this gap 4.03 eV for model **M1**, colorless, and 2.7 eV for model **M4**, highly colored.

The interactions of the model compounds and of the copolymers with different anions are selective and give rise to color changes. The color developed upon addition of F⁻ to aprotic organic solutions containing urea compounds has been precisely described by Esteban-Gómez et al.³⁸ The phenomenon was ascribed to an acid-base reaction and not to a host-guest interaction. Thus, the unsolvated anion behaves as a strong base in organic conditions, causing the deprotonation of the urea group and giving rise to an even stronger ITC. Nevertheless, not all our models experiments color development or variations in solution upon addition of fluoride, showing the complex nature of these kinds of phenomena. This could be partially explained because our systems are more complex as some of the models have -OH or -NH₂ groups capable of interacting with the carbonyl group of the urea and amide moieties and also capable of giving rise to a relatively strong interaction with the fluoride anion through halogen bonds.

Therefore, the model compounds and polymers could serve as "naked eye" sensing materials, allowing for their use in chromogenic sensing devices. As an example, Figure 4 depicts the color changes obtained upon adding fluoride anions to solutions of the model compounds. Further investigations are under progress related to the sensing behavior of the polymers and models both in solution and in the solid state.



FIGURE 7 Fluorescence images of solutions of models **M1**, **M2**, **M3**, **M4**, **M5**, and **M6** and (from left to right) in DMSO (2 \times 10⁻³ M): (a) upper photograph: without added anion; (b) lower photograph: with a fluoride concentration of 10⁻² M (fluoride added as [CH₃ CH₂)₃]₄NF).

Some of the model compounds and copolyamides are highly fluorescent, exhibiting intense blue to orange fluorescence both in solution and in the solid state as a thin film or powder (Figs. 5 and 6). The nature of the fluorescence behavior could be somewhat related with the ICT. Thus, the highly fluorescent models (**M3** and **M5**) show a nearly colorless pattern in DMSO solution, probably indicating that the strong ICT could give rise to an energy-wasting pathway quenching the fluorescence of the fluorescence.³⁹

The fluorescence emission maxima of the copolymers and models are shown in Table 3. Notably, the spectra of copolyamide films show a broad emission band and a significant bathochromic emission shift compared with the solution emission spectra, highlighting the influence of the solid state in the fluorescence behavior of these materials. These redshifts were attributed to packing and orientation effects in the local geometry of the polymer chains in the dense films.^{40,41}

The addition of selected anions caused different variations in the emission spectra depending on the coupled anion/copolymer or anion/model, potentially allowing for the design of fluorogenic sensors with low detection limits. As an illustrative example of the fluorogenic sensing of the fluoride ions, Figure 7 depicts the naked eyed fluorescence changes observed upon addition of the anion to the copolymer solutions under UV irradiation at 366 nm.

CONCLUSIONS

This work described the synthesis and characterization of six new functional fluorescent copolyamides and their corresponding polyamide models, bearing urea in the bulky pendant structure along with the fluorene derivatives. The preparation of a parent copolyamide permits the modification of the copolymer structure by easy and clean reactions to yield high-performance polyamides with "a la carte" fluorescent and chromogenic properties. The general inherent difficulties associated with the achievement of clean and high-yield chemical modification of the polymers were overcome by initially optimizing the chemicals and reaction conditions with polyamide model compounds. The influence of the chemical structure of the pendant fluorene core was addressed in terms of thermal properties, solubility, and water uptake.

In short, the clean and easy preparation of functional polymers by polymer modification reactions produced a family of high-value high performance materials starting with a single parent polymer. The characteristics of these materials make them useful for cutting-edge technologies based on the fluorescence of the pendant fluorene moiety and to the host behavior of the urea motif in fluorescent sensing of analytes or hybrid LUCO—LED systems. Further investigations are in progress.

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