



**HAL**  
open science

## Polyamide model compound containing the urea group as selective colorimetric sensing probe toward aromatic diamines.

Noelia San-Jose, Ana Gomez-Valdemoro, Veronica Calderon, Jose L de La Peña, Felipe Serna, Felix C Garcia, Jose Miguel Garcia

► **To cite this version:**

Noelia San-Jose, Ana Gomez-Valdemoro, Veronica Calderon, Jose L de La Peña, Felipe Serna, et al. Polyamide model compound containing the urea group as selective colorimetric sensing probe toward aromatic diamines.. *Supramolecular Chemistry*, 2009, 21 (05), pp.337-343. 10.1080/10610270701882193 . hal-00513528

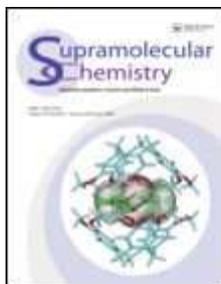
**HAL Id: hal-00513528**

**<https://hal.science/hal-00513528>**

Submitted on 1 Sep 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Polyamide model compound containing the urea group as selective colorimetric sensing probe toward aromatic diamines.**

Journal:	<i>Supramolecular Chemistry</i>
Manuscript ID:	GSCH-2007-0144.R2
Manuscript Type:	Full Paper
Date Submitted by the Author:	11-Dec-2007
Complete List of Authors:	San-Jose, Noelia; Universidad de Burgos, Quimica Gomez-Valdemoro, Ana; Universidad de Burgos, Quimica Calderon, Veronica; Universidad de Burgos, Quimica de la Peña, Jose; Universidad de Burgos, Quimica; Universidad de Burgos, Quimica Serna, Felipe; Universidad de Burgos, Quimica Garcia, Felix; Universidad de Burgos, Quimica Garcia, Jose; Universidad de Burgos, Quimica
Keywords:	polyamide model compounds, amine sensing, urea, host-guest chemistry
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.	
Scheme1.cdx Scheme2.cdx	



1  
2  
3 **Polyamide model compound containing the urea group as selective colorimetric**  
4 **sensing probe toward aromatic diamines.**  
5

6 Noelia San-José, Ana Gómez-Valdemoro, Félix Clemente García, Felipe Serna, José  
7 Luis de la Peña, José Miguel García.\*  
8  
9

10  
11  
12 **Graphical abstract**  
13

14  
15  
16  
17 A novel polyamide model compounds for aromatic diamine colorimetric sensing is  
18 described. Colorless solutions of the models in NMP develop a yellow-greenish, red or  
19 blue color upon addition of *ortho*, *meta* or *para*-phenylenediamine, respectively, while  
20 remain silent upon addition of other aliphatic and aromatic amines and diamines.  
21  
22  
23  
24



1  
2  
3 **Polyamide model compound containing the urea group as selective colorimetric**  
4 **sensing probe toward aromatic diamines.**  
5  
6  
7

8 Noelia San-José, Ana Gómez-Valdemoro, Verónica Calderón, José Luis de la Peña  
9 Felipe Serna, Félix Clemente García, and José Miguel García.\*  
10

11 Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Plaza de  
12 Misael Bañuelos s/n, E-09001 Burgos, Spain.  
13  
14

15  
16  
17  
18  
19  
20  
21 **Correspondence to:**

22 Prof. Dr. José Miguel García.

23 Facultad de Ciencias.

24 Departamento de Química.

25 Universidad de Burgos.

26 Plaza de Misael Bañuelos s/n.

27 09001 Burgos, Spain.

28 Telephone number: + 34 947 25 80 85

29 Fax: + 34 947 25 88 31

30 Email: [jmiguel@ubu.es](mailto:jmiguel@ubu.es)

31 <http://www2.ubu.es/quim/quimorg/polimeros/polimeros.htm>  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 **Polyamide model compound containing the urea group as**  
5 **selective colorimetric sensing probe toward aromatic**  
6 **diamines.**  
7  
8  
9

10  
11 **Noelia San-José, Ana Gómez-Valdemoro, Verónica Calderón, José Luis de la Peña**  
12 **Felipe Serna, Félix Clemente García, and José Miguel García.\***  
13

14  
15 <sup>a</sup> *Departamento de Química. Facultad de Ciencias. Universidad de Burgos. Plaza de*  
16 *Misael Banuelos s/n. E-09001 Burgos. Spain. Tel.: +34 947 258 085; fax: + 34 947 258*  
17 *831; E-mail: jmiguel@ubu.es*  
18  
19  
20  
21

---

22  
23 **Abstract**  
24

25 A colorimetric diacid monomer for aromatic diamine sensing containing the urea  
26 binding site have been synthesized and characterized. A colour development from  
27 colourless to blue, brown or yellow was observed upon addition of *meta*, *para* or  
28 *ortho*-phenylenediamine, respectively, to polar aprotic organic solvent solutions of the  
29 monomers. The solutions remained colourless upon addition of other amines or  
30 diamines. The model polyamide compound derived from the diacid monomer maintain  
31 the colorimetric sensing selectivity toward the aromatic diamines, so the polyamides  
32 derived from the diacid monomer described herein are supposed to retain the ability to  
33 interact selectively with the aromatic diamines, so cheap future sensing devices could be  
34 built by means of easy-to-use naked-eye polyamide film chemosensor or by  
35 incorporating a polyamide coating in the end of an optic fibre connected to a portable  
36 diode array visible detector.  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52

53  
54 **Keywords:** polyamide model compounds; amine sensing; urea; host-guest chemistry.  
55  
56  
57  
58  
59  
60

## 1. Introduction

The development of selective and sensitive materials for sensing anion, cation and neutral molecules is a topical research area [1-4]. Interest in materials that behave as hosts toward guest molecules arises from the importance attached to easy and quick detection and quantification of chemicals in environmental, biological and chemical processes. Thus, detection and quantification of chemicals, such as aromatic diamines, have a certain technological importance. Compounds such as *ortho*, *meta* or *para*-phenylenediamines are important intermediates in engineering polymers and composites, aramid fibres, hair dyes, adhesive and rubber chemicals, textile dyes, ion exchange and decolorizing resins, urethanes, petroleum additives and corrosion inhibitors, and are also important building blocks in heterocyclic chemistry.

The reported examples of chromogenic sensing systems for neutral molecules, i.e. amines, generally rely on the reactivity of certain functional groups [5-11]. Thus, amine colorimetric signalling is generally based on a chemodosimeter approach involving a nucleophilic substrate attack that generates a new fluorescent unit [5]. Although in itself an interesting approach, its disadvantage lies in its poor selectivity due to the possibility of an attack by other nucleophiles, including the water OH<sup>-</sup> groups. Moreover, the signalling events of these systems are usually shown near the UV zone, and rarely at more interesting longer wavelengths, in the visible region. Additionally, these optical transducers are generally designed to detect a set of related compounds which share the same functional group, without selectivity. Thus, the most interesting systems for amine detection are molecules that interact with amines by means of hydrogen bonds, which produce variations in the fluorescence or in the UV/Vis spectra of the system [12-14].

In previous articles we have reported on the synthesis and characterization of polymer materials with the following host units: crown ether [15-17]; urea [18,19]; or

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

pyrylium [20,21], along with their interaction with cations [22-25], anions [20,21] or gas molecules [26]. This work concerns the development of polymeric optical transducers of the presence of intimately related compounds. We therefore report herein a polyamide model compound (Scheme 1, Figure 1) that exhibit colorimetric sensing selectivity toward isomeric aromatic diamines (Figure 2). Thus, the models probably mimic the polyamides, polymers derived from the diacid monomers (**I**), which are intermediates in the synthesis of the models. The polymeric materials are supposed to retain the ability to interact selectively with these diamines, such that cheap future sensing devices might well take the form of user-friendly naked-eye polyamide film sensors or might incorporate a polyamide coating at the end of an optic fibre connected to a portable UV/Vis diode-array detector. Moreover, as the aromatic polyamide are a class of polymer of great technological importance, due mainly to its mechanical and electrical properties and its outstanding thermal resistance, the sensing devices prepared with these materials could be utilized in a wide range of thermal and mechanical conditions, in smooth to extreme environments, making them unique components in the control of industrial chemical concentrations, i.e. in air, gases, inside reactors, or waste products, and also in environmental protection and occupational safety and health, through determination of pollutant concentrations.

## 2. Experimental

### 2.1. Materials

All materials and solvents were commercially available and were used as received, unless otherwise indicated. N-Methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide were vacuum-distilled twice, over phosphorus pentoxide, and then stored over 4Å molecular sieves. Lithium chloride was dried at 400°C for 12 hours prior to use. Triphenylphosphite (TPP) was vacuum distilled twice over calcium hydride, and

1  
2  
3 then stored over 4Å molecular sieves. Pyridine was dried under reflux over sodium  
4  
5 hydroxide for 24 hours, and distilled over 4Å molecular sieves. *m*-Phenylenediamine  
6  
7 (MPD) was commercially available and purified by double vacuum sublimation.  
8  
9

## 10 2.2. Synthesis and characterization of the polyamide model compound

11  
12  
13 *5-(3-phenylureido)isophthalic acid (I)*. 50 mmol of 5-aminoisophthalic acid were  
14  
15 dissolved in 10 ml of *N,N*-dimethylacetamide in a 50 mL Erlenmeyer flask fitted with  
16  
17 mechanical stirring. Afterwards, 50 mmol of phenylisocyanate were added dropwise.  
18  
19 The solution was stirred at room temperature for 24 h, and then precipitated in 300 mL  
20  
21 of slightly acidified water. The product, 5-(3-phenylureido)isophthalic acid, was filtered  
22  
23 off, and washed thoroughly with distilled water. The crude product was recrystallized  
24  
25 from ethanol. Yield: 88%. M.p.: 281 °C (d). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sup>6</sup>): δ (ppm),  
26  
27 13.27 (s, 2H); 9.18 (s, 1H); 8.78 (s, 1H); 8.33 (m, 2H); 8.14 (m, 1H); 7.52 (dd, 2H);  
28  
29 7.33 (t, 2H); 7.03 (t, 1H). <sup>13</sup>C-NMR (100,6 MHz, DMSO-*d*<sup>6</sup>): δ (ppm), 167.62; 153.50;  
30  
31 141.50; 140.37; 132.72; 129.79; 124.21; 123.64; 122.16; 119.54. EI-LRMS *m/z*: 300  
32  
33 (*M*<sup>+</sup>; 4), 207 (59), 190 (35), 181 (50), 164 (14), 119 (59), 93 (100), 66 (32). FTIR  
34  
35 [Wavenumbers (cm<sup>-1</sup>): ν<sub>N-H</sub>: 3286; ν<sub>acid, O-H</sub>: broad band (3657-2752); ν<sub>C=O</sub>: 1716,  
36  
37 1646; δ<sub>N-H</sub>: 1603; ν<sub>Ar C=C</sub>: 1567.  
38  
39  
40  
41  
42  
43  
44

45  
46 *N,N'*-diphenyl-5-(3-phenyl-ureido)-isophthalamide (II). In a 50 mL three-necked  
47  
48 flask fitted with mechanical stirring, 20 mmol of aniline, 10 mmol of 5-(3-  
49  
50 phenylureido)isophthalic acid and 1.4 g of lithium chloride were dissolved in a mixture  
51  
52 of 6 mL of pyridine, 22 mmol of TPP and 20 mL of NMP. The solution was stirred and  
53  
54 heated at 110 °C under a dry nitrogen blanket for 4 hours. The system was then cooled  
55  
56 at room temperature and the solution precipitated in 300 mL of methanol to render a  
57  
58 swollen fibrous precipitate. The model obtained was filtered off and washed with  
59  
60

1  
2  
3 distilled water and acetone and then extracted with acetone for 24 h in a Soxhlet, and  
4  
5 dried in a vacuum oven at 80 °C overnight. Yield: 94%. It was obtained as a  
6  
7 semicrystalline solid (55 % crystallinity) that crystallized at 169 °C. M.p.: 256 °C. The  
8  
9 IR-FT and the <sup>1</sup>H and <sup>13</sup>C NMR spectra, along with the signals assignment are shown in  
10  
11 Figure 1. LRMS (70 eV, EI), *m/z* (%): 331 (55), 239 (100), 185 (11), 119 (60), 93 (62),  
12  
13 65 (16). Elemental analysis for C<sub>27</sub>H<sub>22</sub>N<sub>4</sub>O<sub>3</sub> (450.50): calc (%) C 71.99, H 4.92, N  
14  
15 12.44; found (%) C 71.73, H 5.07, N 12.19.

### 20 2.3. Measurements and Instrumentation

21  
22  
23 <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian Inova 400 spectrometer  
24  
25 operating at 399.92 and 100.57 MHz, respectively, with deuterated dimethylsulfoxide  
26  
27 (DMSO-d<sub>6</sub>) as solvents.  
28

29  
30  
31 FAB and low resolution electron impact mass spectra (EI-LRMS, 70 eV) were  
32  
33 carried out on a Micromass AutoSpect Waters mass spectrometer.  
34

35  
36 Infrared spectra (FT-IR) were recorded with a Nicolet Impact spectrometer.  
37

38  
39 UV/Vis spectra were record with a Varian Cary3-Bio UV-Vis  
40  
41 spectrophotometer.  
42

43  
44 Elemental analyses were performed on a LECO CHNS-932 microanalyzer.  
45

46  
47 Thermogravimetric analysis (TGA) data were recorded under a nitrogen  
48  
49 atmosphere on a Mettler-Toledo TGA\SBTA851 analyzer from 5 mg of sample at a  
50  
51 scan rate of 10 °C/min.  
52

### 53 3. Results and discussion

54  
55  
56  
57  
58  
59  
60

1  
2  
3 The new model polyamide compound (**II**) and its diacid monomer precursor (**I**)  
4 contain an urea group and two aromatic amide linkages, in which the carbonyl groups of  
5 the amides act as a slightly electron withdrawing group and the urea moiety as a slightly  
6 electron donating one. Although the urea group has been exploited in compounds that  
7 mainly exhibit their sensing behaviour toward anions [27-31] and hardly ever toward  
8 cations [32], their strong hydrogen-bonding ability, both in solution and in the solid state,  
9 either with other groups or alone - i.e. to give clathrates - opens the door to specific  
10 interactions with neutral molecules in the field of molecular recognition, or host-guest  
11 chemistry [33-35]. Moreover, aromatic urea derivatives have shown the ability to form  
12 oligomeric assemblies, or capsules, in which guests can be encapsulated in solution, and  
13 the complex capsules persist even in the solid state, as demonstrated by X-ray analysis  
14 [36-38].

15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32 The diacid monomer (**I**) and the polyamide model compound (**II**) are  
33 straightforward prepared (Scheme 1) by cheap and conventional methods which render  
34 the products with high yield and purity. As an illustrative example, the characterization of  
35 **II** is depicted in Figure 1, the spectra showing the high purity of the model.

36  
37  
38  
39  
40  
41  
42 The chromogenic sensing properties of model polyamide compounds **II** in DMA  
43 solutions were tested in the presence of certain aliphatic and aromatic amines and  
44 diamines. In a typical assay, 43 mg of the proper diamine (0.23 mmol) were added to a  
45 colourless DMA solution (1 mL) of the proper **II** (0.1 M). The system was sealed and  
46 stored in the dark for 24 h. The results are shown in Figure 1. The DMA solution of **II**  
47 remained silent in the presence of a wide set of different amines, whereas **II** was highly  
48 selective toward diamines derived from benzene, and developed either a yellow-greenish,  
49 blue or red colour upon addition of *ortho*, *meta* or *para*-phenylenediamine, respectively  
50 (Figure 1).  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

The interaction between **II** and *meta*-phenylenediamine (MPD) in DMSO solution was studied using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. By starting with a 0.1 M solution of **II** in DMSO- $d_6$ , and gradually adding MDP, the variations in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of both chemicals in response to the increasing concentration of MPD were evaluated. The MPD/**II** concentration ratio ( $C_{A_0}/C_{M_0}$ ) ranged from 0.1/1 to 10/1. For each sample, the chemical shift of amidic and urea protons and the carbonyl carbon of the urea and amide groups were compared to their values in a pure **II** in DMSO- $d_6$  solution. The chemical shift variations of the amine proton of the MPD were analyzed by the same procedure. The chemical shifts of the analyzed protons and carbons in **II** increases with the increased concentration of MPD, and it approaches a constant value. In the case of the diamine proton, the chemical shift decreased when the concentration of this compound increased in the sample, and it approached the chemical shift of pure MPD in DMSO- $d_6$  solution. Thus, the interaction between **II** and MPD, responsible for the chemical shift variations, can be described as a binding of a diamine, A, to the model, M, according to the equilibrium described by Equation 1 [39].



The chemical shift variations were analyzed by using a two-site model, which assumes that the experimental chemical shift is the sum of two chemical shifts: the first one for the compound when it interacts with the other,  $\delta_{\text{bound}}$ , and, the second for the compound when it is free in the solution,  $\delta_{\text{free}}$ . This model is described by the relationship expressed in Equation 2,

$$(\delta_{\text{obs}})_i = x_{\text{free}} (\delta_{\text{free}})_i + x_{\text{bound}} (\delta_{\text{bound}})_i \quad (2)$$

where,  $i$  is the atom whose chemical shift is considered to evaluate the molar fraction,  $\delta_{\text{obs}}$  is the observed chemical shift at a given concentration,  $x_{\text{bound}}$  and  $x_{\text{free}}$  are the

molar fractions of the bound and free compounds, respectively,  $\delta_{\text{free}}$  corresponds to the chemical shift of the pure solutions and  $\delta_{\text{bound}}$  is given by Equation 3. Hence,  $\delta_{\text{bound}}$  can be estimated by the extrapolation of observed chemical shift data to zero and infinite concentrations of MPD.

$$(\delta_{\text{bound}})_{i,A} = (\delta_{\text{obs}})_{i,A} \Big|_{C_{A_0} \rightarrow 0} \quad ; \quad (\delta_{\text{bound}})_{i,M} = (\delta_{\text{obs}})_{i,M} \Big|_{C_{A_0} \rightarrow \infty} \quad (3)$$

Once the  $(\delta_{\text{bound}})_i$  is estimated by Equation 3, the molar fractions of free MPD and **II** can be calculated by applying Equation 2. Figure 2 shows a plot of the molar fraction of both compounds as a function of the concentration ratio.

Taking material balance into account (equation 4), the stoichiometry of interaction between model **II** and MPD can be obtained by plotting the bound molar fraction relation,  $(1-x_M)/(1-x_A)$ , versus the initial concentration ratio. The slope of the linear fit corresponds to the model polyamide compound **II**/MPD interaction relation,  $m/n$ . The regression results appear to indicate an interaction **II**/MPD of 4/1 (Table 1).

$$C_{A_n M_m} = \frac{C_{A_0}}{n} (1-x_A) = \frac{C_{M_0}}{m} (1-x_M) \quad \therefore \quad \frac{(1-x_M)}{(1-x_A)} = \frac{m}{n} \left( \frac{C_{A_0}}{C_{M_0}} \right) \quad (4)$$

Capsules formed through head-to-tail arrays of 12 hydrogen bonds formed by urea containing molecules have previously been described in solution, through a self assembly processes [36-38]. In our systems, we obtained a complex constituted by four molecules of model polyamide compound **II** and one molecule of MPD. On the basis of this result, we conjecture that the formation of a capsule-like complex of four molecules of the model compound occurs with alternating up-and-down pendant urea groups encapsulating a diamine derived from benzene. The capsule might be maintained in solution by a belt of 8 head-to-tail array hydrogen bonds, and two caps, up and down the belt, of amide-amide

1  
2  
3 hydrogen-bond linkages. The cavity inside the capsule should have a shape in which guest  
4  
5 diamines will fit, which in turn will establish new hydrogen bonds with urea and amide  
6  
7 groups, thereby modifying the electronic structure of the supramolecular entity, and  
8  
9 giving rise to a charge transfer complex with the concomitant development of colour.  
10  
11 Further studies should be carried out to establish the structure of these complexes. The  
12  
13 development of colour should also be investigated in depth, because it is not  
14  
15 instantaneous. One possible hypothesis might be that decomposition species of the  
16  
17 diamines could also be partially responsible, although the experimental fact that the  
18  
19 polymerization of **I** with freshly purified MPD by double sublimation (Scheme 2)  
20  
21 developed a deep blue colour instantaneously make us reject this possibility.  
22  
23  
24  
25  
26

27  
28 In order to get insight into the **II**/diamine complex structure we have tried to  
29  
30 obtain a monocrystal to study the structure of the complex in the solid state by the X-  
31  
32 Ray diffraction technique, but we have not succeeded. Anyway, we have obtained nice  
33  
34 white crystals upon crystallization of a mixture of **II** and MPD in THF/hexane (in this  
35  
36 solvent mixture the development of colour was not observed) with a composition, as  
37  
38 determined by  $^1\text{H}$  NMR, of approx. 4 molecules of the model **II** and 1 of the diamine.  
39  
40 This fact does really not mean that the complex is a capsule, although it support it,  
41  
42 because it also could be another kind of structure, but it indicates that a supramolecular  
43  
44 arrangement can be isolated even in the solid state. Additionally, the low resolution  
45  
46 FAB<sup>+</sup> mass spectra of these crystals shows peaks at 559, 1008, 1458, 1909, the mass of  
47  
48 1:1, 2:1, 3:1 and 4:1 **II**/MPD complex, respectively, and although mass spectrometry  
49  
50 only reflects the properties of gas-phase species, the correlation with the solid state is  
51  
52 often reliable.  
53  
54  
55  
56  
57

58  
59 Moreover, the mass spectra of model **II** indicates the presence of dimeric, trimeric  
60  
and tetrameric species (FAB<sup>+</sup>,  $m/z = 901, 1350, 1799$ ), indicating that the intermolecule

1  
2  
3 interaction of **II** is strong enough to give rise to supramolecular assemblies. Furthermore,  
4 the amidic and ureidic proton resonances of model **II** (protons *a*, *c* and *e* in Scheme 1) in  
5  
6  
7  
8  $^1\text{H}$  NMR experiments (using DMSO- $d_6$  as solvent) depends on the concentration. Thus,  
9  
10 the increasing concentration give rise to a highfield shifting of these protons, indicating  
11  
12 that the amide and urea groups interact in solution by means of hydrogen bonds, even in a  
13  
14 competitive polar solvent as DMSO.  
15

16  
17  
18 From a macroscopic point of view, the concentration of MPD in solution could be  
19  
20 followed colorimetrically adding a fixed quantity of **II**. Thus, the titration of MPD with  
21  
22 the model **II** is shown in Figure 4, showing that the UV-Vis Absorbance (600 nm) of a  
23  
24 solution of **II** in DMA increases proportionally to the **II**/MPD concentration ratio.  
25  
26

27  
28 Upon adding the proper diamine to a solution of the model the colour  
29  
30 development is mainly observed in polar aprotic solvents, as DMA, N-methylpyrrolidone,  
31  
32 dimethylformamide and dimethylsulfoxide.  
33  
34

35  
36 In preliminary experiments, we have observed that the polymerization of **I** with  
37  
38 MPD in NMP (Scheme 2) take place initially with the development of a dark blue and a  
39  
40 red colour, respectively, that disappeared over time, owing to decreasing diamine  
41  
42 concentrations as polymerization progressed. This means that the diacid **I** also behaves as  
43  
44 an aromatic diamine sensor and, more importantly, that the diamine concentrations can be  
45  
46 monitored online during the polymerization process. This is a significant fact because it  
47  
48 could be employed to control synthetic procedures for aramids, which are of a certain  
49  
50 economic significance, as well as other industrial processes involving diamines.  
51  
52  
53

54  
55 The polyamide **III** is an aromatic polyamide considered as a high performance  
56  
57 material with good chemical resistance and outstanding mechanical behaviour [18].  
58  
59 Therefore, further work will be carried out to analyze the sensing characteristics of the  
60  
polyamides. Preliminary experiments have shown that DMA solutions of the polyamide

1  
2  
3 **III**, derived from **I**, retain the sensing behaviour of the models **II**. Thus, polymer **III** could  
4  
5 be mixed with other polymers, or it could be crosslinked to yield a network in order to  
6  
7 elaborate film strips to naked-eye detection of aromatic amines or to manufacture  
8  
9 detecting devices based on UV/Vis spectroscopy. As an illustrative comparison of the  
10  
11 diacid monomer, the model and the polyamide properties, Figure 5 shows the TGA  
12  
13 patterns of all the compounds, showing all the same initial decomposition temperature,  
14  
15 between 200 and 250 °C, typical of the thermal degradation of the urea group.  
16  
17  
18  
19

#### 20 4. Conclusion

21  
22  
23 In summary, we have synthesized and characterized a model polyamide  
24  
25 compound, which contains urea binding sites, for the colorimetric sensing of aromatic  
26  
27 diamines. The design of these receptors is intended to give them the ability to selectively  
28  
29 recognize and sense the phenylene diamine isomers. Three colour developments from  
30  
31 colourless to yellow-greenish, blue and red were observed upon addition of either *ortho*,  
32  
33 *meta* or *para*-phenylenediamine, respectively, to solutions of the model polyamide  
34  
35 compounds (**II**) in polar aprotic organic solvents. The solutions remained colourless upon  
36  
37 addition of other amines or diamines. Further research will be carried out to extend the  
38  
39 sensing capabilities of these model molecules in water environments and also to study the  
40  
41 sensing capabilities of dense or semipermeable membranes obtained from the  
42  
43 corresponding polyamides.  
44  
45  
46  
47  
48

#### 49 Acknowledgements

50  
51  
52 The financial support provided by the Ministerio de Educación y Ciencia – Feder  
53  
54 (MAT2005-01355) and the Junta de Castilla y León - Feder (BU003A05) is gratefully  
55  
56 acknowledged.  
57  
58  
59

#### 60 References

- 1  
2  
3  
4  
5  
6 [1] Trinchì, A.; Muster, T.H. *Supramol. Chem.* **2007**, *19*, 431-445.  
7 [2] Kim, S.K.; Kim, H.N.; Xiaoru, Z.; Lee, H.N.; Lee, H.N.; Soh, J.H.; Swamy, K. M.  
8 K.; Yoon, J. *Supramol. Chem.* **2007**, *19*, 221-227.  
9 [3] Martínez-Máñez R.; Sancenón F. *Chem. Rev.* **2003**, *103*, 4419-4476.  
10 [4] Martínez-Máñez R.; Sancenón, F. *J. Fluoresc.* **2005**, *15*, 267-285.  
11 [5] Chen P.; Novotny M.V. *Anal. Chem.* **1997**, *69*, 2806-2811.  
12 [6] Mohr G.J.; Demuth C.; Spichiger-Keller U.E. *Anal. Chem.* **1998**, *70*, 3868-3873.  
13 [7] Sasaki S.; Kotegawa Y.; Tamiaki H. *Tetrahedron Lett.* **2006**, *47*, 4849-4852.  
14 [8] Feuster E.K.; Glass T.E. *J. Am. Chem. Soc.* **2003**, *125*, 16174-16175.  
15 [9] Mohr G.J.; Tirelli N.; Lohse C.; Spichiger-Keller U.E. *Adv. Mater.* **1998**, *10*, 1353-  
16 1357.  
17 [10] Rose M.J.; Lunte S.M.; Carlson R.G.; Stobaugh J.F. *Anal. Chem.* **1999**, *71*, 2221-  
18 2230.  
19 [11] Liu C.J.; Lin J.T.; Wang S.H.; Jiang J.C.; Lin L.G. *Sens. Actuators B* **2005**, *108*,  
20 521-527.  
21 [12] Jung J.H.; Lee S.J.; Kim J.S.; Lee W.S.; Sakata Y.; Kaneda T. *Org. Lett.* **2006**, *8*,  
22 3009-3012.  
23 [13] Gao T.; Tillman E.S.; Lewis, N.S. *Chem. Mater.* **2005**, *17*, 2904-2911.  
24 [14] Lee, Y.J.; Park, K.D.; Yeo, H.M.; Ko, S.W.; Ryu, B.J.; Nam, K.C. *Supramol.*  
25 *Chem.* **2007**, *19*, 167-173.  
26 [15] Calderón, V.; García, F.; de la Peña, J.L.; Maya E.; García, J.M. *J. Polym. Sci Part*  
27 *A: Polym. Chem.* **2006**, *44*, 2270.  
28 [16] Calderón, V.; García, F.; de la Peña, J.L. Maya, E.M.; Lozano, A.E.; de la Campa,  
29 J.G.; de Abajo J.; García, J.M. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*,  
30 4063.  
31 [17] Calderón, V.; Shwarz, G.; García, F.; Tapia, M.J.; Valente, A.J.M.; Burrows,  
32 H.D.; de la Peña J.L.; García, J.M. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*,  
33 6252.  
34 [18] San-José N.; Gómez-Valdemoro A.; García F.C.; Serna F.; García J.M. *J. Polym.*  
35 *Sci. Part A: Polym. Chem.* **2007**, *45*, 4026-4036.  
36 [19] San-José N.; Gómez-Valdemoro A.; García F.C.; de la Peña J.L.; Serna F.; García  
37 J.M. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 5398-5407.  
38 [20] García-Acosta B.; García F.; García J.M.; Martínez-Máñez R.; Sancerón F.; San-  
39 José N.; Soto, J. *Org. Lett.* **2007**, *9*, 2429-2432.  
40 [21] García F.; García J.M.; García-Acosta B.; Martínez-Máñez R.; Sancerón F.; Soto,  
41 J. *Chem. Commun.* **2005**, 2790-2792.  
42 [22] Calderón, V.; Serna F.; García F.; de la Peña J.L.; García J.M. *J. Appl. Polym. Sci.*  
43 **2007**, *106*, 2875-2884.  
44 [23] Tapia M.J.; Valente A.J.M.; Burrows H.D.; Calderón V.; García F.; García J.M..  
45 *Eur. Polym. J.* **2007**, *43*, 3838-3848.  
46 [24] Rubio F.; García F.; Burrows H.D.; Pais A.A.C.C.; Valente A.J.M.; Tapia M.J.;  
47 García J.M. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 1788-1799.  
48 [25] Tapia M.J.; Burrows H.D.; García J.M.; García F., Pais A.A.C.C. *Macromolecules*  
49 **2004**, *37*, 856-862.  
50 [26] Tiemblo P.; Guzmán J.; Riande E.; García, F.; García J.M. *Polymer* **2003**, *44*,  
51 6773-6780.  
52 [27] Jose D.A.; Kumar D.K.; Ganguly B.; Das A. *Tetrahedron Lett.* **2005**, *46*, 5343-46.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4  
5 [28] Jiménez D.; Martínez-Máñez R.; Sancerón F.; Soto J. *Tetrahedon Lett.* **2002**, *43*,  
6 2823-2825.  
7 [29] Otón F.; Tárraga F.; Velasco M.D.; Espinosa A.; Molina P. *Chem. Commun.* **2004**,  
8 1658-1659.  
9 [30] Xu G.; Tarr M.A. *Chem. Commun.* **2004**, 1050-1051.  
10 [31] Kim Y.J.; Kwak H.; Lee S.J.; Lee J.S.; Kwon H.J.; Nam S.H.; Lee K.; Kim C.  
11 *Tetrahedron* **2006**, *62*, 9635-9640.  
12 [32] Yang H.; Liu Z.Q.; Zhou Z.G.; Shi E.X.; Li F.Y.; Du Y.K.; Yi T.; Huang C.H.  
13 *Tetrahedron Lett.* **2006**, *47*, 2911-2914.  
14 [33] Hollingsworth M.D.; Brown M.E.; Hillier A.C.; Santarsiero B.D.; Chaney J.D.  
15 *Science* **1996**, *273*, 1355-1359.  
16 [34] Harris, K.D.M. *J. Solid State Chem.* **1993**, *106*, 83-89  
17 [35] Steed J.W.; Atwood J.L. *Supramolecular Chemistry*; John Wiley & Sons:  
18 Chichester, 2000; Ch. 5.  
19 [36] Alajarín M.; Pastor A.; Orenes R.A.; Martínez-Viviente E.; Rügger H.; Pregosin  
20 P.S. *Chem. Eur. J.* **2007**, *13*, 1559-1569.  
21 [37] Alajarín M.; Pastor A.; Orenes R.A.; Steed J.W. *J. Org. Chem.* **2002**, *67*, 7091-  
22 7095.  
23 [38] Alajarín M.; Pastor A.; Orenes R.A.; Steed J.W.; Arakawa, R. *Chem. Eur. J.* **2004**,  
24 *10*, 1383-1397.  
25 [39] Jolivalt C.; Böckmann A.; Ries-Kautt M.; Ducruix A.; Guittet E. *Biophys. Chem.*  
26 **1998**, *71*, 221-234.  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## Figure Captions

**Scheme 1.** Synthesis of the diacid monomer (**I**) and the model polyamide compound (**II**).

**Scheme 2.** Polymerization of the diacid monomer (**I**) with *m*-phenylenediamine to yield the polyamide (**III**).

**Figure 1.** Characterization of polyamide model **II**: (a) FTIR, (b)  $^1\text{H}$  NMR, and (c)  $^{13}\text{C}$  NMR. FTIR spectra were recorded on KBr pellets, and DMSO- $d_6$  was used as solvent in the NMR experiments.

**Figure 2.** a) Photograph of **II** solutions in DMA upon addition, from left to right, of ethanolamine, triethylamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 4,4'-diamino-diphenylsulfone, tris-(2-aminoethyl) amine, 1,2-diaminocyclohexane, aniline, *o*-phenylenediamine, *m*-phenylenediamine, and *p*-phenylenediamine. b) UV/Vis spectra of solutions of **II** with *o*-phenylenediamine (yellow-green), *m*-phenylenediamine (blue), and *p*-phenylenediamine (red).

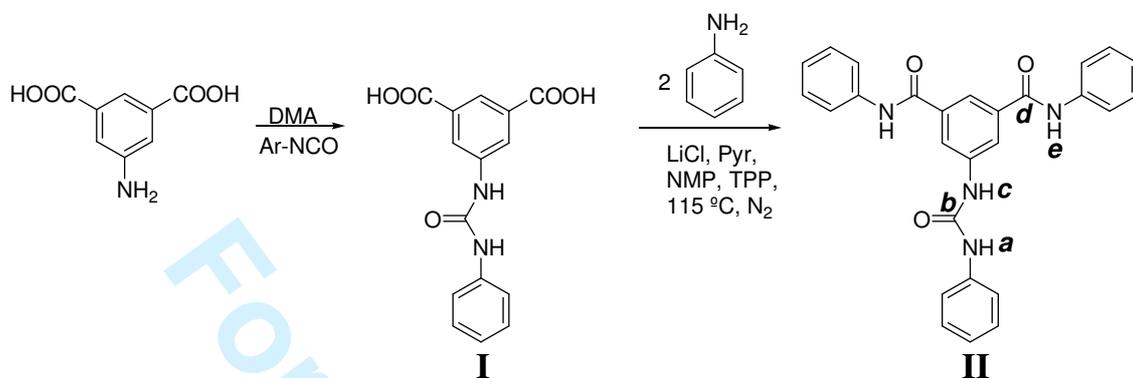
**Figure 3.**  $x_A$  and  $x_M$  vs.  $C_{A0}/C_{M0}$ .  $x_M$  are the averaged values obtained from the chemical shift variation of the amidic and urea protons and carbons of **II** after interaction with MPD (Equation 2).

**Figure 4.** UV-Vis Absorbance (600 nm) of **II** upon exposure to increasing amounts of MPD in DMA.

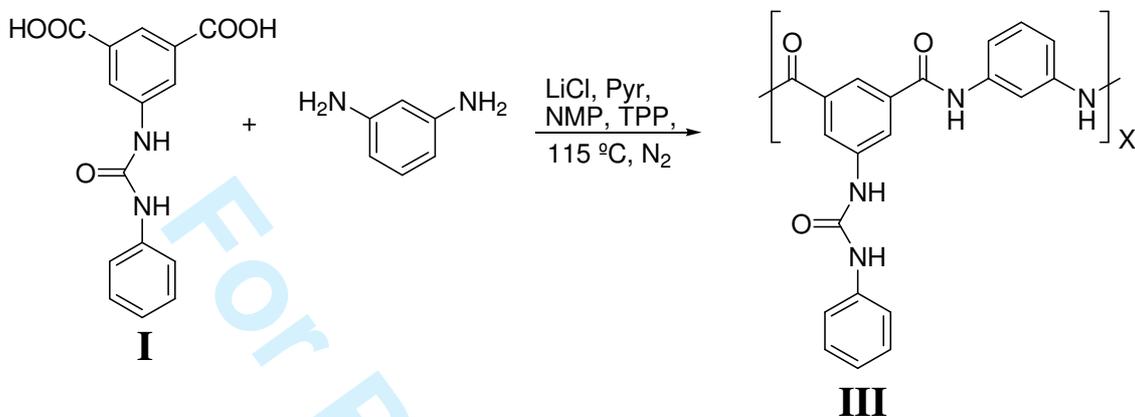
**Figure 5.** TGA of the diacid monomer **I** (dash), model compound **II** (dots) and polyamide derived from the polymerization of the diacid monomer (**I**) and *m*-phenylenediamine (continuous line).

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

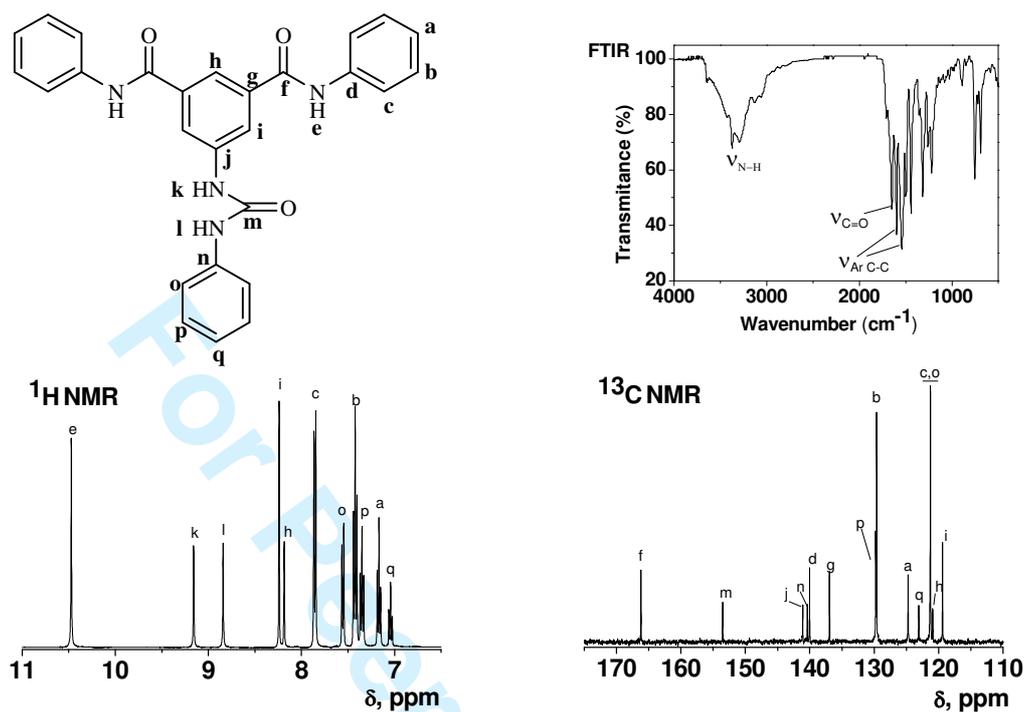
For Peer Review Only



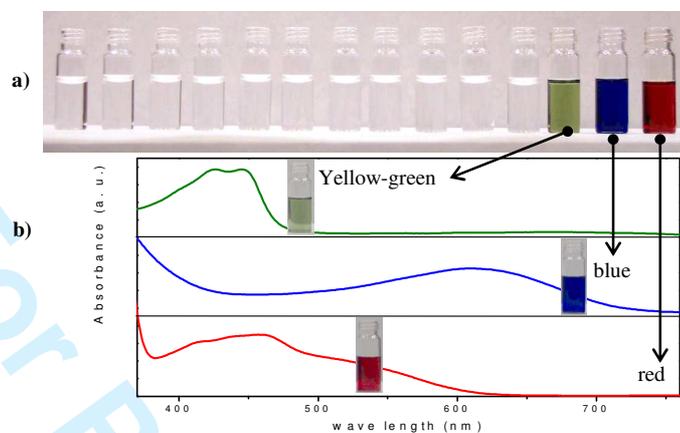
**Scheme 1.** Synthesis of the diacid monomer (I) and the model polyamide compound (II).



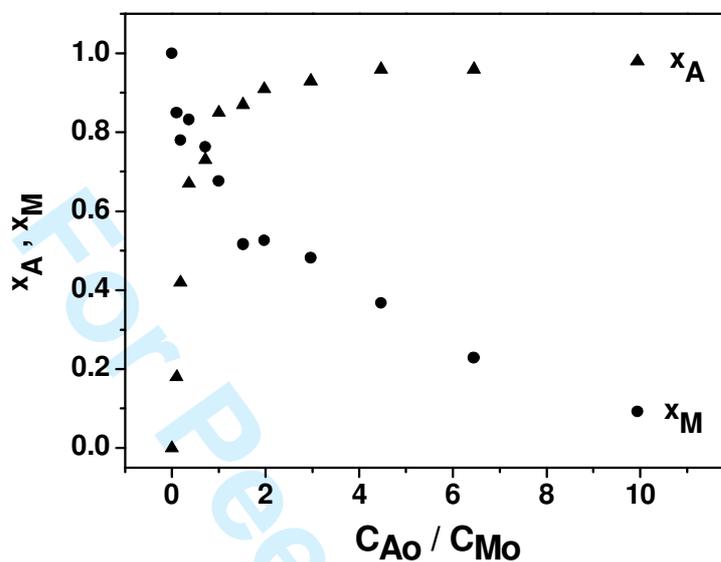
**Scheme 2.** Polymerization of the diacid monomer (I) with *m*-phenylenediamine to yield the polyamide (III).



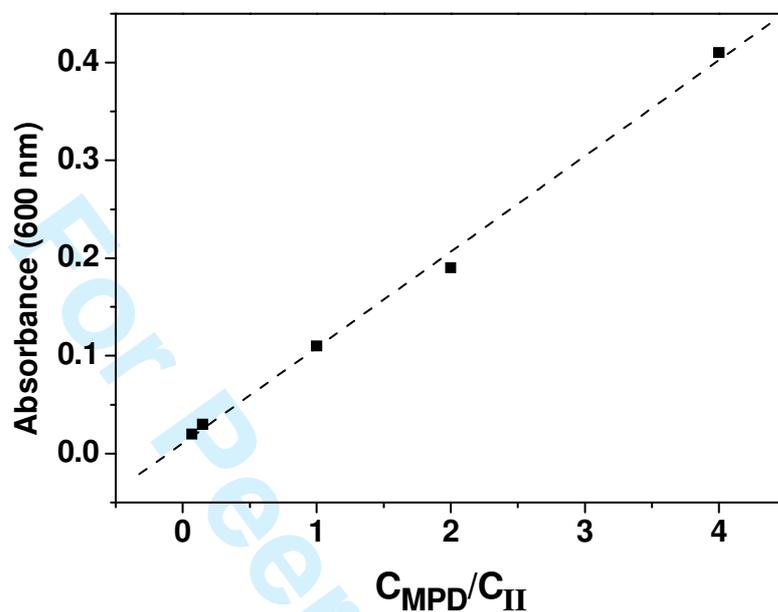
**Figure 1.** Characterization of polyamide model II: (a) FTIR, (b) <sup>1</sup>H NMR, and (c) <sup>13</sup>C NMR. FTIR spectra were recorded on KBr pellets, and DMSO-d<sub>6</sub> was used as solvent in the NMR experiments.



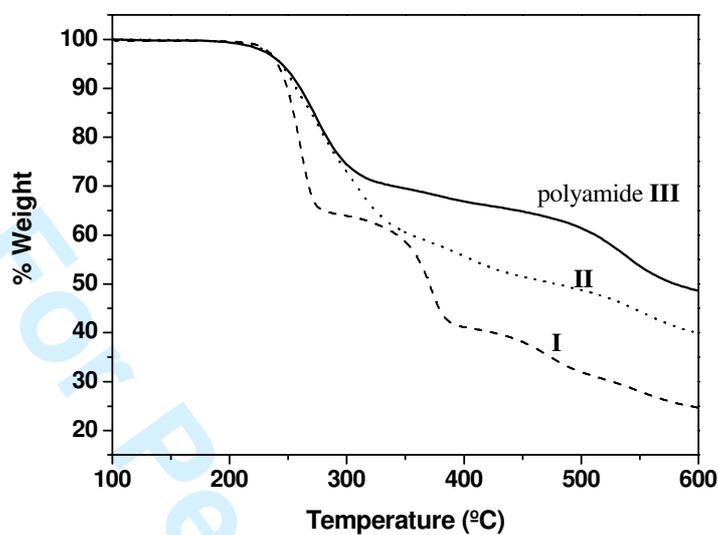
**Figure 2.** a) Photograph of **II** solutions in DMA upon addition, from left to right, of ethanolamine, triethylamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 4,4'-diaminodiphenylsulfone, tris-(2-aminoethyl) amine, 1,2-diaminocyclohexane, aniline, *o*-phenylenediamine, *m*-phenylenediamine, and *p*-phenylenediamine. b) UV/Vis spectra of solutions of **II** with *o*-phenylenediamine (yellow-green), *m*-phenylenediamine (blue), and *p*-phenylenediamine (red).



**Figure 3.**  $x_A$  and  $x_M$  vs.  $C_{Ao}/C_{Mo}$ .  $x_M$  are the averaged values obtained from the chemical shift variation of the amidic and urea protons and carbons of **II** after interaction with MPD (Equation 2).



**Figure 4.** UV-Vis Absorbance (600 nm) of **II** upon exposure to increasing amounts of MPD in DMA.



**Figure 5.** TGA of the diacid monomer **I** (dash), model compound **II** (dots) and polyamide derived from the polymerization of the diacid monomer (**I**) and *m*-phenylenediamine (polyamide **III**, continuous line).

## Tables

**Table 1.** Model polyamide compound-diamine interaction relation ( $\mathbf{II}/\text{MPD} = m/n$ , Equations 1 and 4) as obtained by the linear regression of  $(C_{A0}/C_{M0})$  vs  $(1-x_M)/(1-x_A)$  values, the slope representing the  $\mathbf{II}$  to MPD complex ratio.

Atom used to obtain the molar fraction data (see Scheme 1)	m/n	R <sup>2</sup>
Hc	4.5	0.988
Ha	4.5	0.991
He	4.1	0.973
Cd	3.7	0.974

1  
2  
3 **Polyamide model compound containing the urea group as selective colorimetric**  
4 **sensing probe toward aromatic diamines.**  
5

6  
7 Noelia San-José, Ana Gómez-Valdemoro, Félix Clemente García, Felipe Serna, José  
8 Luis de la Peña, José Miguel García.\*  
9

10  
11  
12 **Graphical abstract**  
13

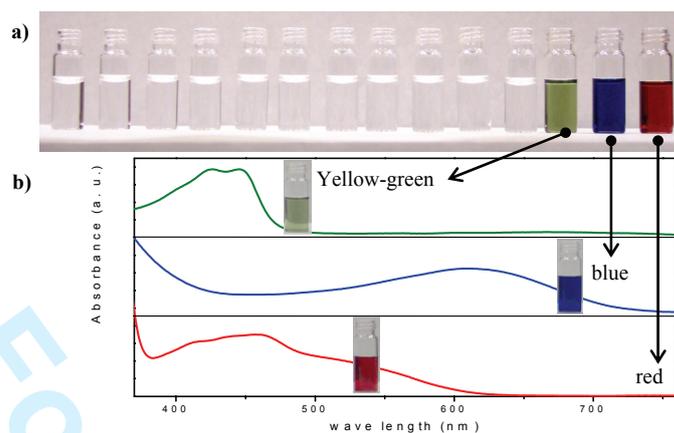
14  
15  
16  
17 A novel polyamide model compounds for aromatic diamine colorimetric sensing is  
18 described. Colorless solutions of the models in NMP develop a yellow-greenish, red or  
19 blue color upon addition of *ortho*, *meta* or *para*-phenylenediamine, respectively, while  
20 remain silent upon addition of other aliphatic and aromatic amines and diamines.  
21  
22  
23  
24



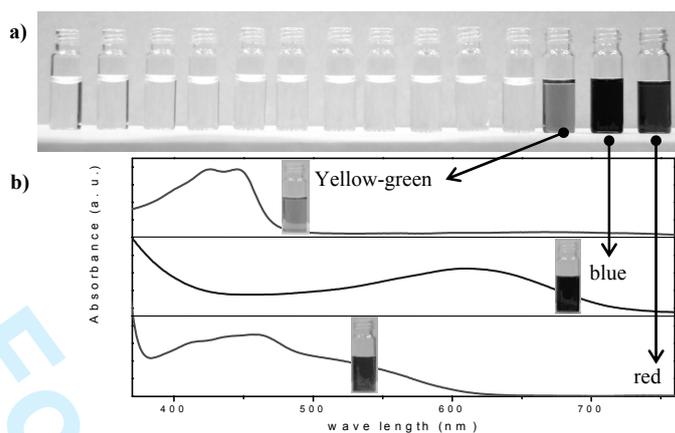
## Tables

**Table 1.** Model polyamide compound-diamine interaction relation ( $\mathbf{II}/\text{MPD} = m/n$ , Equations 1 and 4) as obtained by the linear regression of  $(C_{A0}/C_{M0})$  vs  $(1-x_M)/(1-x_A)$  values, the slope representing the  $\mathbf{II}$  to MPD complex ratio.

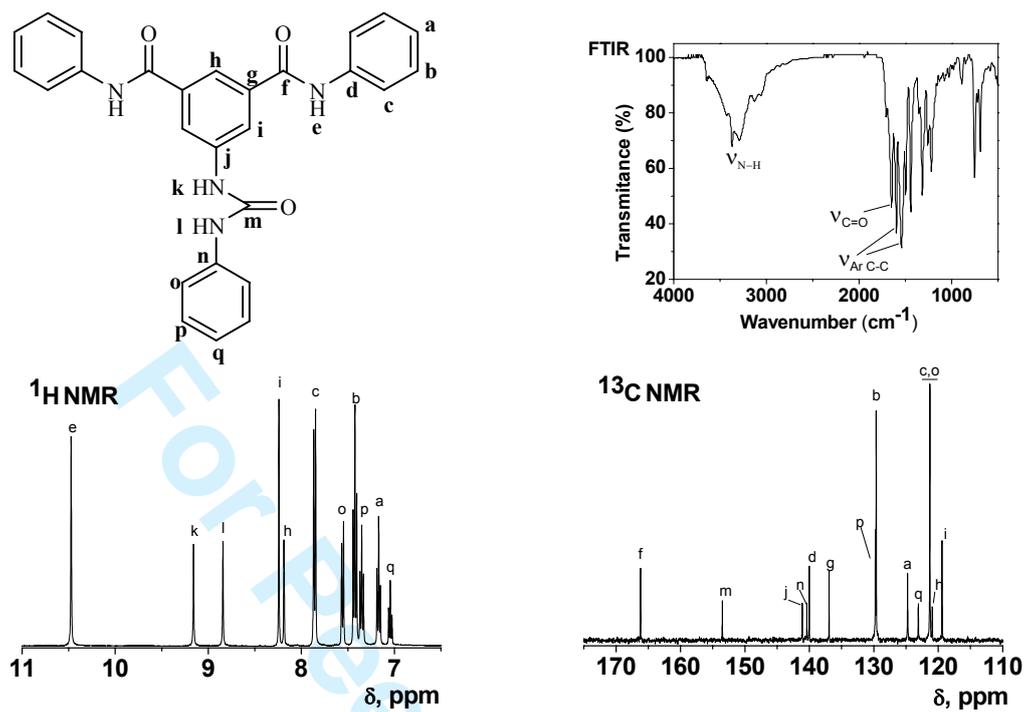
Atom used to obtain the molar fraction data (see Scheme 1)	m/n	R <sup>2</sup>
Hc	4.5	0.988
Ha	4.5	0.991
He	4.1	0.973
Cd	3.7	0.974



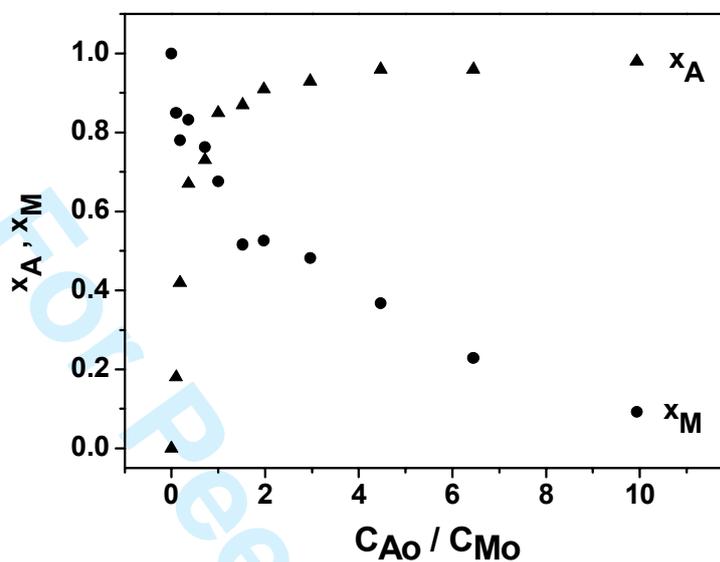
**Figure 2.** a) Photograph of **II** solutions in DMA upon addition, from left to right, of ethanolamine, triethylamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 4,4'-diaminodiphenylsulfone, tris-(2-aminoethyl) amine, 1,2-diaminocyclohexane, aniline, *o*-phenylenediamine, *m*-phenylenediamine, and *p*-phenylenediamine. b) UV/Vis spectra of solutions of **II** with *o*-phenylenediamine (yellow-green), *m*-phenylenediamine (blue), and *p*-phenylenediamine (red).



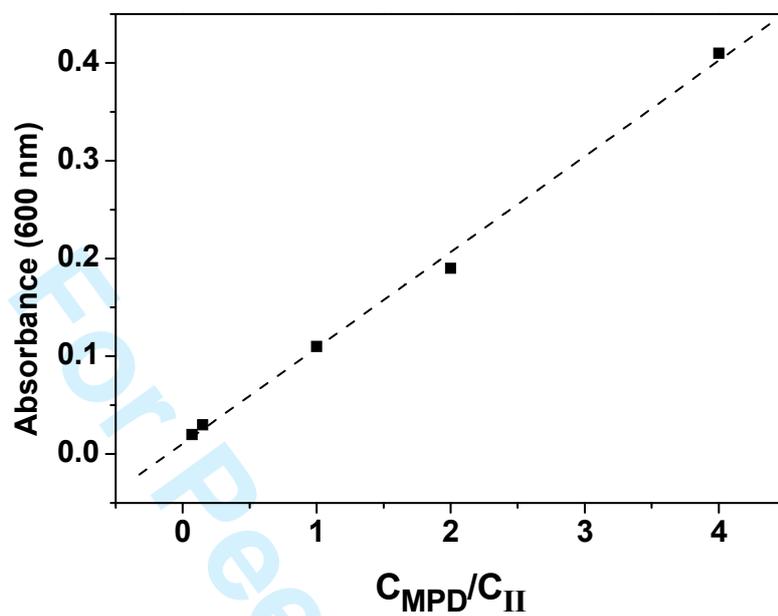
**Figure 2.** a) Photograph of **II** solutions in DMA upon addition, from left to right, of ethanolamine, triethylamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 4,4'-diaminodiphenylsulfone, tris-(2-aminoethyl) amine, 1,2-diaminocyclohexane, aniline, *o*-phenylenediamine, *m*-phenylenediamine, and *p*-phenylenediamine. b) UV/Vis spectra of solutions of **II** with *o*-phenylenediamine (yellow-green), *m*-phenylenediamine (blue), and *p*-phenylenediamine (red).



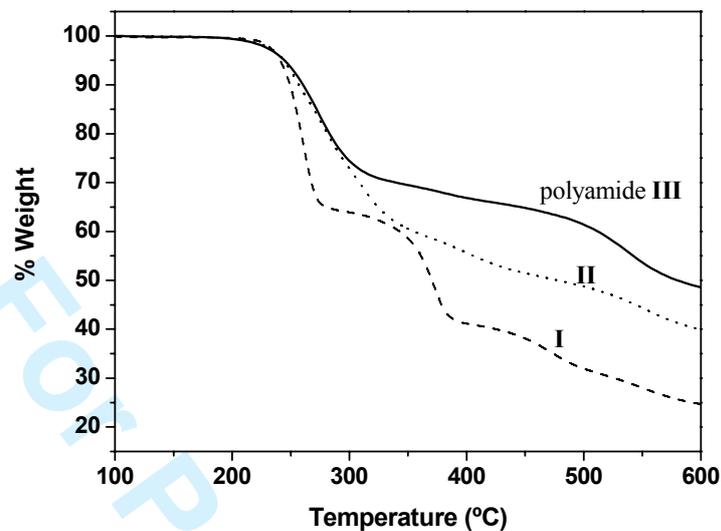
**Figure 1.** Characterization of polyamide model II: (a) FTIR, (b) <sup>1</sup>H NMR, and (c) <sup>13</sup>C NMR. FTIR spectra were recorded on KBr pellets, and DMSO-d<sub>6</sub> was used as solvent in the NMR experiments.



**Figure 3.**  $x_A$  and  $x_M$  vs.  $C_{Ao}/C_{Mo}$ .  $x_M$  are the averaged values obtained from the chemical shift variation of the amidic and urea protons and carbons of **II** after interaction with MPD (Equation 2).



**Figure 4.** UV-Vis Absorbance (600 nm) of **II** upon exposure to increasing amounts of MPD in DMA.



**Figure 5.** TGA of the diacid monomer **I** (dash), model compound **II** (dots) and polyamide derived from the polymerization of the diacid monomer (**I**) and *m*-phenylenediamine (polyamide **III**, continuous line).