

Low Molecular Weight Microfibers with Light Sensing Properties

ANDREI BEJAN^{1*}, DRAGOS PEPTANARIU¹, BOGDAN CHIRICUTA², ELENA BICU³, DALILA BELEF³

¹Petru Poni Institute of Macromolecular Chemistry, 41 Grigore Ghica Voda Alley, 700487, Iasi, Romania

²Apel Laser, 15 Str. Vintila Mihailescu, 060394, Bucharest, Romania

³Alexandru Ioan Cuza University, Department of Organic Chemistry, 11 Carol I Blvd., 700506, Iasi, Romania

Microfibers were obtained from organic low molecular weight compounds based on heteroaromatic and aromatic rings connected by aliphatic spacers. The obtaining of microfibers was proved by scanning electron microscopy. The deciphering of the mechanism of microfiber formation has been elucidated by X-ray diffraction, infrared spectroscopy, and atomic force microscopy measurements. By exciting with light of different wavelength, fluorescence microscopy revealed a specific optical response, recommending these materials for light sensing applications.

Keywords: microfibers, nanofibers, fluorescence, triazoles

Microfibers are materials with great mechanical properties designed for a large scale of high performance applications in optoelectronics and electronics [1,2], biomedicine [3,4], environment protection [5-7], sensing [8], catalysis [9] and so on. The main advantage of the micro/nanofibers is their high surface meaning a large active area. Combining this advantage with other properties, e.g. luminescence, led to high performance materials with higher application potential. Depending on the targeted application, the micro-, nano-fibers are prepared from polymers [10], biopolymers [11] inorganic salts [12], organic blends [13], organic-inorganic composites [14,15] or inorganic-inorganic blends [16]. The latest research revealed the possibility to prepare micro/nanofibers from organic low molecular weight compounds [17-21]. The structural design which appears to facilitate their formation is the presence of flexible spacers as internal building blocks. The obtaining of micro-, nano-fibers from organic low molecular weight compounds offers the advantage of an easier application targeting by tailoring the design by proper chose of the building blocks, an easier purification and so obtaining of microfibers of high purity – requirement especially important for optoelectronics or biomedicine, easy processability from solution and so low cost.

Starting from these premises, we designed a series of low molecular weight compounds comprising three aromatic/heteroaromatic units connected by short aliphatic chains as flexible units. The rational choice of these aromatic moieties is their use in the design of many drugs, due to their therapeutic activity [22-25]. On the other hand, they have potential to promote luminescence properties [26-28]. This paper deals with the study of the obtaining of microfibers from a series of organic low molecular weight compounds and the study of their light sensing properties.

Experimental part

Synthesis

All the compounds used for the microfiber preparation were synthesised in agreement with a procedure reported elsewhere [17, 20].

Equipment and methods

Fourier transformed infrared (FTIR) spectra of the microfibers were performed with a FT-IR Bruker Vertex 70

Spectrophotometer, by ATR technique. FTIR spectra of the studied compounds were also registered in the transmission mode, by using KBr pellets. The spectra have been processed using OPUS 6.5 software.

Crystallographic measurements on the microfibers were measured on an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo K α radiation.

The microfiber morphology was visualized on a field emission Scanning Electron Microscope SEM EDAX – Quanta 200, at accelerated electron energy of 10 KeV. The morphology of the microfibers at nano level has been monitored by atomic force microscopy on a Solver PRO-M, NT-MDT equipment, in semi contact mode.

The fluorescence measurements were done on a Leica DM 2500 microscope, using A, I3, and N2.1 filter cubes, with UV, blue and green excitation wavelengths, respectively. The fiber appearance under bright field has been verified on the same microscope.

Nanofibers preparation

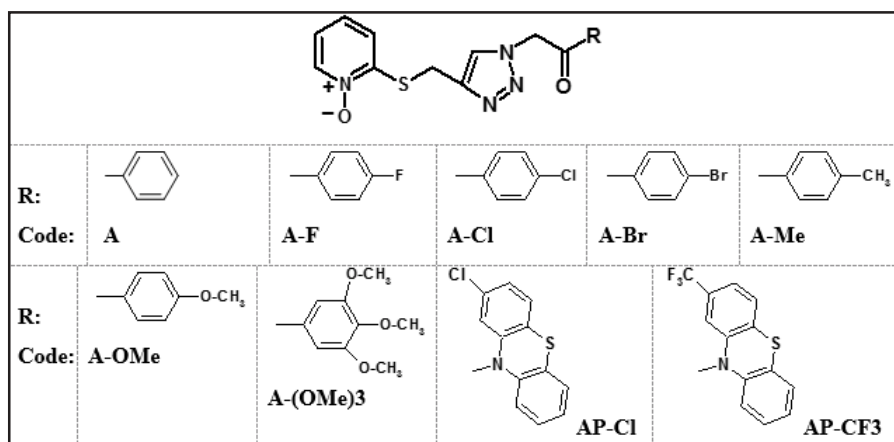
0.2 mL of a 1% solution in DMSO has been poured under vigorous stirring into 0.8 mL chloroform, heptane or water. In all three cases, abundant opalescence suspensions were formed. They were casted onto glass supports and allowed to dry at atmospheric pressure, and further under vacuum.

Results and discussions

A series of organic low molecular weight compounds consisting in a combination of aromatic/heteroaromatic rigid moieties and flexible units (scheme 1) have been synthesised and their ability to form microfibers has been studied in detail. The compounds were prepared according to a synthetic procedure reported elsewhere and their right structure has been confirmed by FTIR and NMR spectroscopy, and elemental analysis [17, 20].

By reprecipitation method from DMSO solution into water, chloroform or heptane nonsolvent (see experimental part), all the studied compounds instantaneously yielded microfibers, as demonstrated by scanning electron microscopy (fig. 1). The fibres have the diameter around 1 μm with a narrow polydispersity, insensitive to the nature of the nonsolvent used in the reprecipitation process. Their length exceeded the size of 400 μm . The microfibers entangled each other giving a non-oven cloth.

* email: bejan.andrei@icmpp.ro



Scheme 1. The structure of the organic low molecular weight compounds

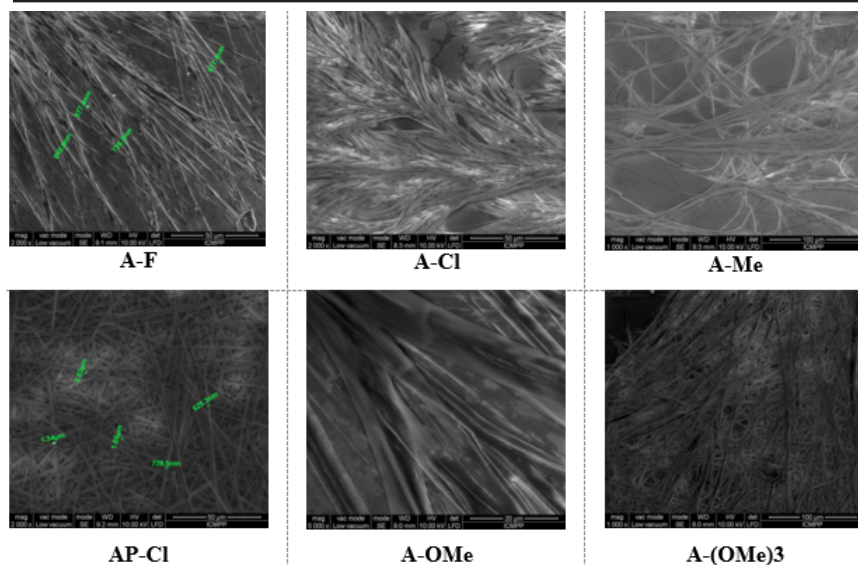


Fig. 1. Representative images of the studied microfibers viewed by SEM

The large dimensions of the microfibers allowed their analysis by optical microscopy, under polarized light or by exciting with UV, blue or green light. Under bright field, the microfibers presented birefringence, indicative of their supramolecular ordering [29, 30]. The analysis of the XRD data confirmed a diffraction pattern characteristic to the highly ordered architectures (fig. 2). The intermolecular distances corresponding to the reflections in the diffractograms have been calculated with the Bragg law. The reflections in the medium angle domain correspond to short interlayer distances from 12.8 to 9.3 Å, while the high density of intense reflections in the wide angle domain correspond to small distances from 6 to 2.7 Å – in agreement with strong intermolecular forces, attributed to the formation of H-bonds and short intermolecular contacts between the electronegative heteroatoms and hydrogen atoms [31-33]. The presence of a high number

of the electronegative heteroatoms in the structure of the studied compounds: three atoms of nitrogen in triazole heterocycle; one atom of nitrogen and one of oxygen in the pyridine-*N*-oxide heterocycle, one atom of oxygen and one of sulphur in the aliphatic spacers, and one atom of nitrogen and one of sulphur in the phenothiazine heterocyclic or halogen atoms or oxygen atom on the aromatic ring, facilitated the physical forces and thus the easy formation of short contacts and hydrogen bonds. Based on these results, the driving force of the microfiber formation has been attributed to a hydrogen bonding network.

The formation of the hydrogen bonds was further demonstrated by FTIR spectra on microfibers. As can be seen in figure 3, along the bands attributed to the vibrations of the chemical linkages of the studied compounds, in the

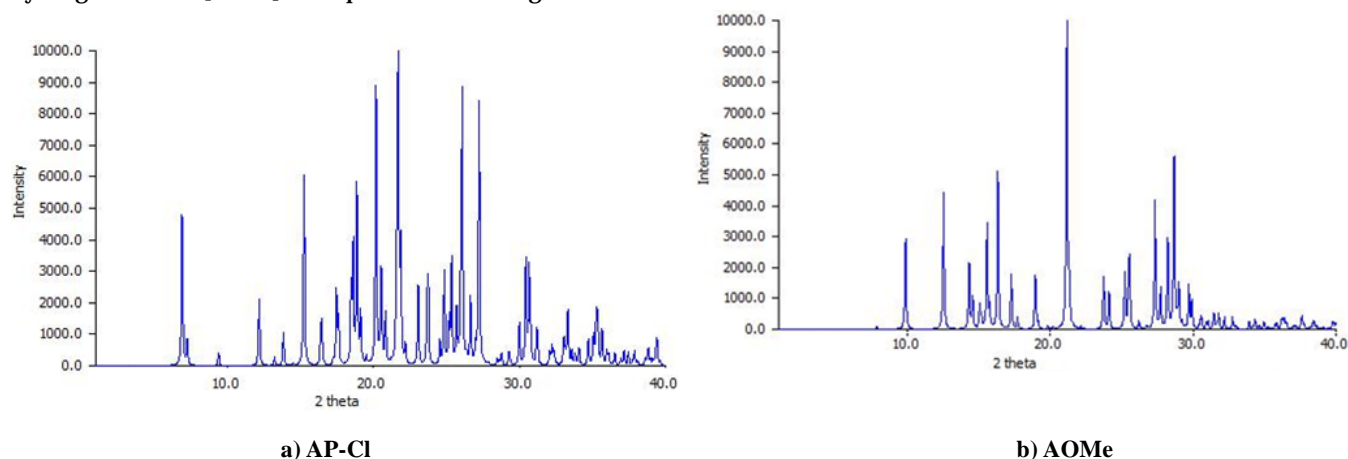


Fig. 2. Representative XRD diffractograms of the studied microfibers

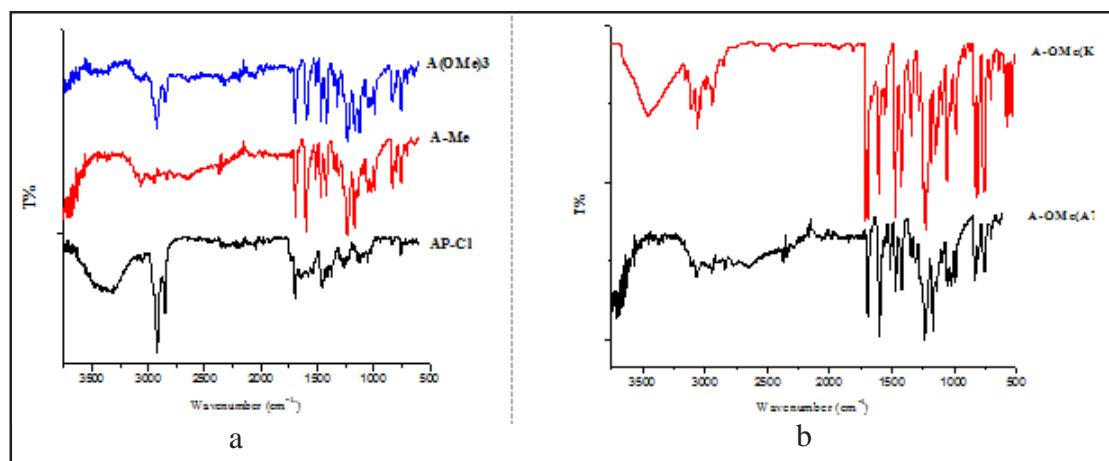


Fig. 3. Representative FTIR spectra of a) the studied microfibers and b) comparative spectra of the microfibers and molecules of the compound A-OMe

3100-3600 cm^{-1} region appeared a broad band attributed to the H-bonds [34]. Moreover, two distinctive overlapped bands can be distinguished in that region, indicating intra- and inter-molecular H-bonds [35, 36]. Comparing the FTIR spectra of the molecules and microfibers of the studied compounds, a significant shift of the spectrum of 23 cm^{-1} to higher wavenumbers was observed indicating electrostatic forces inside the microfibers [19]. Analysing the structure of the compounds, the electrostatic forces were assigned to the strong electric dipole introduced by

the coordinative linkage in pyridine- *N*-oxide moiety. It can be foreseen that these electrostatic forces play an important role in the microfiber formation.

Atomic force microscopy imaging of the microfibers (fig. 4), revealed that they are formed from entangled nanofibers, probably interacting to each other by electrostatic forces [19]. Thus, the microfibers appear as a result of the electrostatic forces between the nanofibers. It can be estimated that due to the high number of heteroatoms, short contacts and hydrogen bonds could be possible between molecules belonging to different

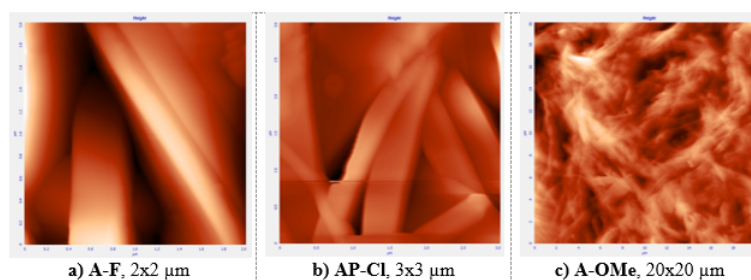
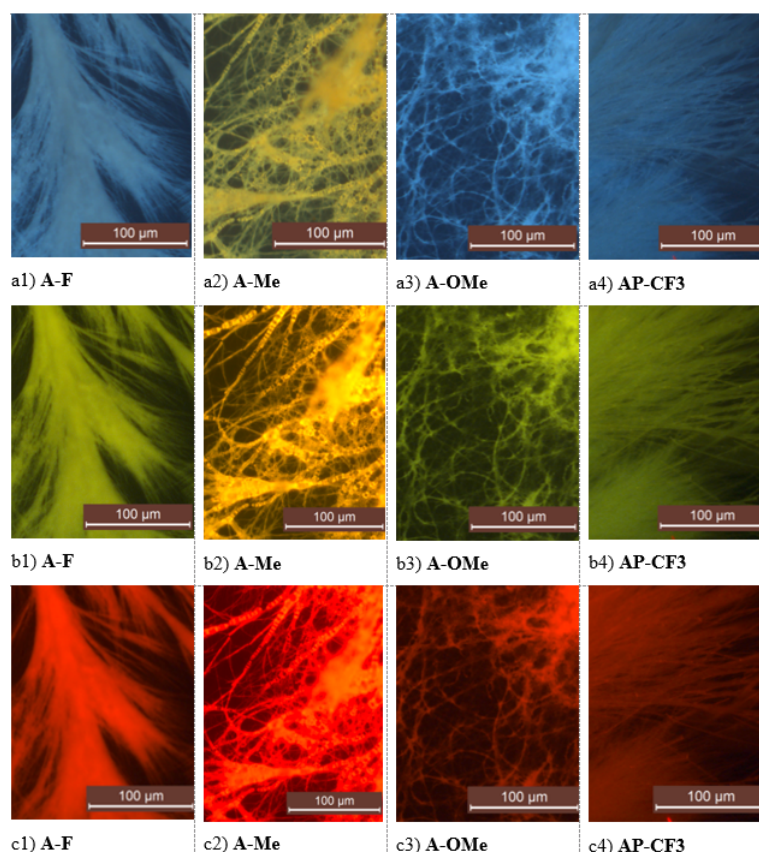


Fig. 4. Representative AFM images of the microfibers

Fig. 5. Representative samples excited with a) UV, b) blue or c) green light



nanofibers. The entanglement of the nanofibers to give microfibers assures a large active surface, beneficial for their further application.

Considering X-ray, FTIR and AFM data, it was concluded that formation of microfibers starting from organic low molecular weight compounds was possible due to multiple synergistic interactions, promoted by the special chemical design of the studied compounds. Thus, the presence of the antagonism flexible - rigid building blocks favoured the self-ordering process, bringing in close positions the electronegative heteroatoms and hydrogen atoms which formed H-bonds. Due to the presence of the flexible aliphatic chains as internal spacers, the obtained tridimensional architectures gain flexibility and became resistant to the breaking, facilitating thus the growing of long nanofibers. The pyridine-*N*-oxide with its strong separation of the electronic charges promoted strong electrostatic forces among the nanofibers giving rise to microfibers.

Light sensing properties

The fluorescence properties of the microfibers were monitored by fluorescence microscopy, by exciting the fibers with UV, blue and green light. Surprisingly, for each exciting wavelength, the samples exhibited different fluorescence as follow. Under UV light, the samples **A-OMe** and **AP-Cl** exhibited yellow fluorescence, whilst all the others exhibited blue fluorescence, **A-(OMe)3** - a deep bright one. Under illumination with blue light, **A-Me** and **AP-Cl** samples have yellow-orange fluorescence, the samples containing methoxy units - shiny fluorescent green one, while the others exhibited green-yellowish emission. And finally, excited with green light, all the samples displayed red fluorescence. Representative fluorescence images were given in figure 5.

Conclusions

Microfibers from organic low molecular weight compounds were prepared by simple reprecipitation technique. The microfibers with diameter around 1 μm are formed from entangled nanofibers due to strong electrostatic forces introduced by the presence of pyridine-*N*-oxide moiety. Excited with light of various wavelength, the microfibers showed different fluorescence. The combination of fluorescence properties and large active surface endow the studied microfibers with capability to change their photophysical properties under environmental triggers, making them promising candidates for sensing applications.

Acknowledgements: This publication is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 667387 WIDESPREAD 2-2014 SupraChem Lab and was also supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI - UEFISCDI, project number PN-III-P3-3.6-H2020-2016-0011, within PNCDI III.

References

1. RAKHI, R.B., CHEN W., CHA D., ALSHAREEF H. N., Nano Lett., **12**, 2012, p. 2559
2. LIU X., LIU Y., SUN W., WANG J., HUANG Z., Liq. Cryst., **40**(2), 2013, p. 249

3. KIDOAKI, S., KWON, I.K., MATSUDA, T., Biomaterials, **26**, 2005, p. 37
4. BECHIR, E.S., PACURAR, M., HANTOIU, T.A., BECHIR, A.M., SMATREA, O., BURCEA, A., GIOGA, C., MONEA, M., Mat. Plast., **53**, no. 1, 2016, p. 104
5. ZHANG J. SEEGER S., Adv. Funct. Mater., **21**, 2011, p. 4699
6. CONSTANDACHE, O., CEREMPEI, A., MURESAN, R., SANDU, I.C.A., MURESAN, A., SANDU I., Mat. Plast., **52**, no. 1, 2015, p. 24
7. CECLAN V.A., BERE P., BORZAN M., GROZAV S., BORZAN C., Mat. Plast., **50**, no. 2, 2013, p. 79
8. REYES, C.G., SHARMA, A., LAGERWALL, J.P.F., Liq. Cryst., **43**(13-15), 2016, p. 1986
9. RADU, C.D., SANDU, I., DIACONESCU, R., BERCU, E., ALDEA, H.A., Rev. Chim. (Bucharest), **65**, no. 7, 2014, p. 797
10. PICKEN S.J., SIKKEMA D.J., BOERSTOEL H., DINGEMANS T.J., ZWAAG S., Liq. Cryst., **38**(11-12), p. 1591
11. MUNTEAN, S.G., SIMU, G., SFARLOAGA, P., BOLOGA, C., Rev. Chim. (Bucharest) **61**, no. 1, 2010, p. 70
12. HOU H., GAO F., WEI G., WANG M., ZHENG J., TANG B., YANG W., Cryst. Growth Des., **12**, 2012, p. 536
13. CHINO M., KITANO K., TANAKA K., AKIYAMA R., Liq. Cryst., **35**(10), 2008, p. 1225
14. TERCUI, O.M., CURTU, I., Mat. Plast., **49**, no. 2, 2012, p. 114
15. GONCALVES G., MARQUES P.A.A., NETO C.P., TRINDADE T., PERES M., MONTEIRO T., Cryst. Growth Des., **9**(1), 2009, p. 386
16. LIU C., HE M., LU X., ZHANG Q., XU Z., Cryst. Growth Des., **5**(4), 2005, p. 1399
17. MARIN L., SHOVA S., DUMEA C., BICU E., BELEI D., Cryst. Growth Des., DOI: 10.1021/acs.cgd.7b00351
18. ZHAO M., ZHAO Y., ZHENG L., DAI C., Chem. Eur. J., **19**, 2013, p. 1076
19. LIN X., ZHONG A., CHEN D., ZHOU Z., HE B.J., J. Appl. Polym. Sci., **87**, 2003, p. 369
20. BELEI D., DUMEA C., BICU E., MARIN L., RSC Adv., **5**, 2015, p. 8849
21. HAN M., CHO S.J., NORIKANE Y., SHIMIZU M., KIMURA A., TAMAGAWA T., SEKI T., Chem. Commun., **50**, 2014, p. 15815
22. AILINCAI D., MARIN L., SHOVA S., TUCHILUS, C., CR Chim., **19**, 2016, p. 556
23. DUMITRIU G.-M., GHINET A., BICU E., RIGO B., DUBOIS J., FARCE A., BELEI D., Bioorg. Med. Chem. Lett., **24**, 2014, p. 3180
24. ZHOU C.-H., WANG Y., Curr. Med. Chem., **19**, 2012, p. 239
25. MFUH A.M., LARIONOV O.V., Curr. Med. Chem., **22**(24), 2015, p. 2819
26. ZABULICA A., BALAN M., BELEI D., SAVA M., SIMIONESCU B.C., MARIN L., Dyes Pigm., **96**, 2013, p. 686
27. ZHANG L., HU W., YU L., WANG Y., Chem. Commun., **51**, 2015, p. 4298
28. MARIN L., ZABULICA A., SAVA M., Soft. Mater., **11**, 2013, p. 32
29. ZABULICA A., PERJU E., BRUMA M., MARIN L., Liq. Cryst., **41**(2), 2014, p. 252
30. MARIN, L., ARVINTE, A., Mat. Plast., **50**, no. 1, 2013, p. 23
31. ZVONICEK V., SKOREPOVA E., DUSEK M., BABOR M., ZVATORA P., SOOS M., Cryst. Growth Des., **17**(6), 2017, p. 3116
32. MARIN L., van der LEE A., SHOVA S., ARVINTE A., BARBOIU M., **39**, 2015, p. 6404
33. BEJAN A., SHOVA S., DAMACEANU M.D., SIMIONESCU B.C., MARIN L., Cryst. Growth Des., **16**, 2016, p. 3716
34. MARIN L., MORARU S., POPESCU M.-C., NICOLESCU A., ZGARDAN C., SIMIONESCU B.C., BARBOIU M., Chem. Eur. J., **20**, 2014, p. 4814
35. IFTIME M.-M., MORARIU S., MARIN L., Carbohydr. Polym., **165**, 2017, p. 39
36. MARIN L., PERJU E., Phase Transit., **82**, 2009, p. 507

Manuscript received: 4.07.2017