“Click” Chemistry for Facile Immobilization of Iron Phthalocyanines onto Electrospun Nanofiber Surface

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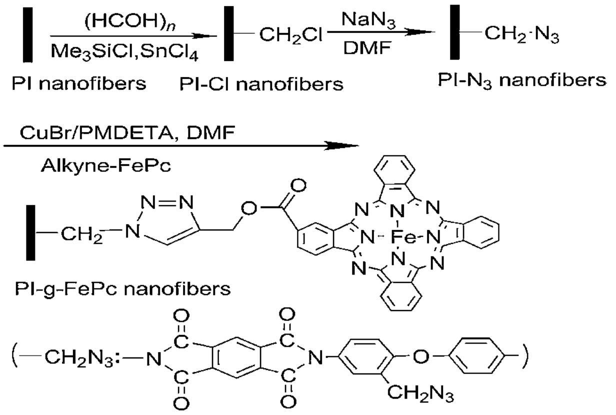
We have developed a facile and efficient methodology to prepare iron phthalocyanine-coated nanofibers by combining electrospinning and Cu(I)-catalyzed 1,3-dipolar Huisgen cycloaddition of azides and alkynes.

Electrospinning is being widely investigated as a simple and robust technique for the production of nano- and microfibers of various materials and with properties tailored for use in diverse applications, ranging from filtration media and tissue engineering to photovoltaics or photocatalysis.[1] During the past few years, a number of important advances in the technique have been reported, such as fiber alignment, composite nanofibers, the exploitation of precursor routes for the production of inorganic nanofibers, and coaxial electrospinning of different polymers, or even of preparation of three-dimensional nanofibrous tubes. Functionalization of nanofibers is a key challenge given the broad range of applications of nanofibers in biology, nanomedicine, the energy, and environment. Up to now, nanofibrous materials with reinforcing, superhydrophobic, and catalytic properties have been reported, nevertheless, ensuring specific functionality to nanofibers is still interesting.[1b]

It is well known that phthalocyanines (Pc) are planar, two-dimensional aromatic molecules, able to self-assemble into stacks through p–p supramolecular interactions. These macrocycles possess electrical and outstanding optical properties that make them perfect building blocks for incorporation into multifunctional materials.[2] However, the system efficiency is greatly limited by the dye aggregation, due to enhanced self-quenching of the excited complex. In this regard, incorporation of Pc species into a nanoscale surface like nanofibers may be a good idea to retard the dye aggregation and, consequently, accelerate the photocatalytic reaction or photoelectric conversion efficiency. To the best of our knowledge, not much work on this subject has been published in the literature. Combining the merits of electrospinning with the bioinspired applications of Pc may generate functionalized nanofibers for multiple purposes.

Recently, “click” chemistry has attracted significant attention in polymer and materials science. Click chemistry, established by Sharpless and co-workers, is an efficient tool for carrying out polymerizations as well as for modifications of macromolecules and solids.[3] In particular, Cu(I)-catalyzed click reaction results in 1,3-dipolar cycloaddition between azides and alkynes even under mild conditions, and the reaction provides products stereoselectively with high yields, produces inoffensive by-products, and is insensitive to oxygen and water.[3a] Click chemistry has been used successfully for the preparation of well-defined structural polymer-grafted nanoparticles, films, carbon nanotubes, and fullerenes.[3b] Hence, click chemistry is used as an ideal tool for immobilization of Pc onto electrospun nanofiber surface. To this end, we have prepared polyimide (PI) nanofibers bearing azide groups allowing the attachment of 2-propynyl phthalocyanine iron (alkyne–FePc) via click reaction. The experimental procedures are shown in Scheme 1.



Scheme 1. Synthetic routes for the preparation of PI-g–FePc nanofibers, via click chemistry.

In general, three processes are needed in sequence for the preparation of Pc-grafted PI nanofibers: alkyne–FePc preparation, azide-decorated PI nanofibers preparation and click coupling. In our previous work, PI–Cl nanofibers was prepared by combining electrospinning and a simple one-step chloromethylation process.[4] In this method, a polyamic acid (PAA) produced from pyromellitic dianhydride and 4,4′-oxydianiline in dimethylacetamide (DMAc) was synthesized by polycondensation. PI nanofibers were prepared via electrospun PAA, followed by thermal imidization. The present chloromethylation was conducted under relatively mild conditions in a one-step synthesis with a mixture of paraformaldehyde [$(HCOH)_n$], chlorotrimethylsilane (Me_3SiCl), and stannic chloride ($SnCl_4$). The PI–Cl nanofibers were then reacted with an excess of NaN_3 to produce azide-decorated PI nanofibers ($PI–N_3$).[4]

The alkyne–FePc was prepared via cyclotetramerisation, followed by esterification. The preliminary report shows the synthetic method of the target unsymmetrical phthalocyanines with a single carboxyl group.[4] The study was based on statistical condensations involving a trimellitic anhydride and phthalic anhydride. Thus, 2-carboxyphthalocyanine iron was prepared by a cyclotetramerisation of phthalic anhydride and trimellitic anhydride in a 7:1 ratio in the presence of urea, anhydrous iron(II) chloride, and ammonium molybdate. Alkyne–FePc was prepared via the reaction between the hydroxy groups of 2-propynyl alcohol and the carboxylic acid groups of 2-carboxyphthalocyanine iron in the presence of both DCC and DMAP.[4] The reaction produced an alkyne-terminated phthalocyanine for click reaction.

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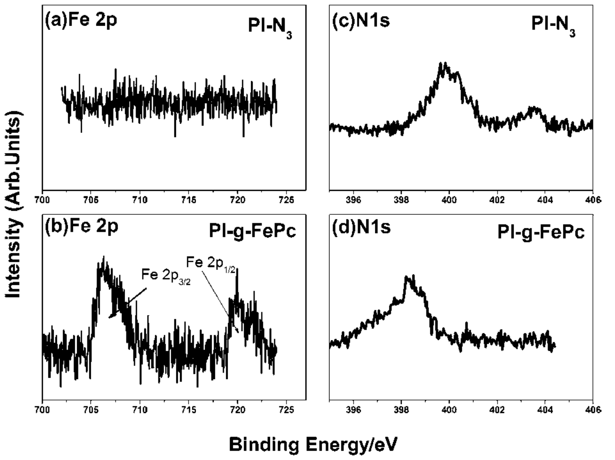

Figure 1. XPS Fe 2p spectra of PI–N_3 (a) and PI-g–FePc (b) nanofiber surface; N 1s spectra of PI–N_3 (c) and PI-g–FePc (d) nanofiber surface.

The functionalization of PI nanofibers (PI-g–FePc) was achieved via click coupling of the azide-decorated PI nanofibers and alkyne–FePc.[4] The PI–N_3 and PI-g–FePc nanofibers were characterized by X-ray photoelectron spectroscopy (XPS). The presence of FePc on the PI nanofiber surface was confirmed by the XPS 2p peaks for iron. Figure 1 shows the XPS Fe 2p core-level spectra of PI–N_3 and the PI-g–FePc nanofiber surface, and reveals Fe $2p_{3/2}$ and $2p_{1/2}$ signals at binding energies (BEs) of about 707 and 720 eV on the PI-g–FePc nanofiber surface, respectively, which is characteristic of Fe 2p spectra. This indicates that FePc was immobilized onto the PI nanofiber surface.

The XPS N 1s results in Figures 1c and 1d reveal additional evidence of 1,2,3-triazole formation on PI surfaces. Peaks appear at 399.7 and 403.5 eV, as expected for azide groups on the surface (Figure 1c). The peak splitting indicates the presence of two nitrogen species at the azide-decorated PI surface, which reflects the differently charged nitrogen atoms in the azide groups. However, after the click reaction, these two peaks disappeared, only a single peak is evident at about 398 eV (Figure 1d), which is characteristic of N 1s spectra of nitrogen from 1,2,3-triazole and Pc, indicating the immobilization of FePc onto the PI nanofiber surface.[5] Grafting yield was defined as $(W_a - W_b)/W_b$, where W_a and W_b were the weight of the dry nanofibers after and before grafting the nanofibers. This value for PI-g–FePc is about 24%.

A microstructural examination was carried out by SEM to evaluate the effect of the surface functionalization of PI nanofibers with FePc by click chemistry (Figure 2). The images showed that pristine PI nanofibers (Figure 2a) were much smoother than those of PI-g–FePc. As observed in Figure 2b, SEM confirmed (1) an increase in the average diameter of the nanofibers and (2) the presence of a rough surface morphology with many small grainy deposits on the surface of PI nanofibers, indicating that the present reaction immobilizes a dense FePc layer onto the PI nanofibers.

Figure 3 shows UV–vis absorption spectra of alkyne–FePc in dilute DMF solution, PI and PI-g–FePc thin films on quartz. PI nanofibers exhibit a very broad and only weak peak at about 330 nm. The large peak in the region of 530–750 nm corresponds to a HOMO–LUMO transition (Q-band). The Q-band in the dilute DMF solution is split in two, with contributions from both monomer absorption (661 nm) and aggregate absorption (629 nm) (Figure 3a).[6] After FePc was immobilized onto the nanofiber surface, it existed predominately in a form of monomer. The aggregate absorption was red shifted to about 660 nm, suggesting a significant enhancement in the dye disassociation (Figure 3b).

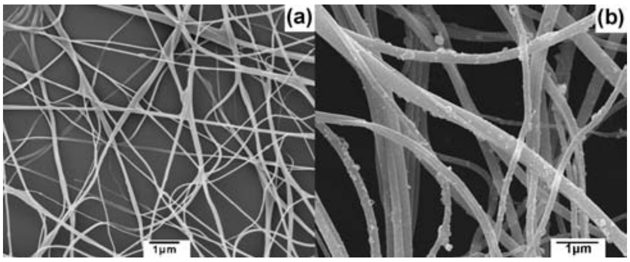

Figure 2. SEM images of pristine PI nanofibers (a) and PI-g–FePc (b).

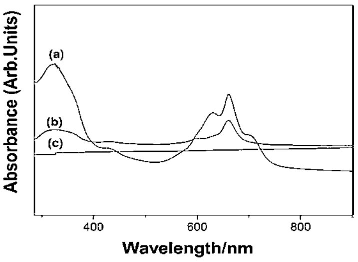

Figure 3. UV–vis absorption spectra of: (a) alkyne–FePc in dilute DMF solution, (b) PI-g–FePc, and (c) PI thin films.

In conclusion, a new approach based on click chemistry has been developed for immobilization of FePc onto electrospun nanofiber surface. As click reactions are modular, highly tolerant toward other functional groups, and high yielding, a large number of functional polymer nanofibers should be easily accessible by using this synthetic approach. Further efforts are currently under way in our group to prepare related devices for photovoltaic and photocatalytic applications.

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References and Notes

1. a) Y. Dzenis, *Science* **2004**, *304*, 1917. b) A. Greiner, J. H. Wendorff, *Angew. Chem., Int. Ed.* **2007**, *46*, 5670.
2. G. Torre, G. G. Claessens, T. Torres, *Chem. Commun.* **2007**, 2000; X. Huang, F. Q. Zhao, Z. Y. Li, L. Huang, Y. W. Tang, F. S. Zhang, C. H. Tung, *Chem. Lett.* **2007**, *36*, 108.
3. a) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.* **2001**, *40*, 2004; P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Frechet, K. B. Sharpless, V. V. Fokin, *Angew. Chem., Int. Ed.* **2004**, *43*, 3928. b) W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2007**, *28*, 15.
4. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
5. A. Devadoss, C. E. D. Chidsey, *J. Am. Chem. Soc.* **2007**, *129*, 5370.
6. P. J. Camp, A. C. Jones, R. K. Neely, N. M. Speirs, *J. Phys. Chem. A* **2002**, *106*, 10725.

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