

# Asymmetric Bilayer Muscles: Cooperative Actuation, Dynamic Hysteresis, and Creeping in NaPF<sub>6</sub> Aqueous Solutions

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Three bilayer muscles [polypyrrole–paraphenolsulfonic acid/polypyrrole–dodecylbenzenesulfonic acid (PPy–HpPS/PPy–DBS) asymmetric bilayer, PPy–HpPS/tape, and PPy–DBS/tape] were characterized during potential cycling in NaPF<sub>6</sub> aqueous solutions. In parallel, the angular displacement of the muscle was video-recorded. The dynamo-voltammetric (angle–potential) and coulo-dynamic (charge–potential) results give the reaction-driven ionic exchanges in each PPy film. Electrochemical reactions drive the exchange of anions from the PPy–HpPS layer and cations from the PPy–DBS layer. This means that both layers from the asymmetric bilayer follow complementary

volume changes (swelling/shrinking or shrinking/swelling), owing to complementary ionic exchanges (entrance/expulsion) driven by the bilayer oxidation or reduction. The result is a cooperative actuation; the bending amplitude described by the asymmetric bilayer muscle is one order of magnitude larger than those attained from each of the conducting polymer/tape muscles. The cooperative actuation almost eliminates creeping effects. A large dynamical hysteresis persists, which can be attributed to an irreversible reaction of the organic acid components at high overpotentials.

## 1. Introduction

Actuators, or artificial muscles, based on conducting polymers (CPs), and other electrochemically active organic and carbon-based materials, constitute the base for the development of promising polymeric sensing motors, tools for surgeons, or zomorphic and anthropomorphic soft robots.<sup>[1–10]</sup> They are electrochemical devices; the CP oxidation/reduction drives the exchange of ions and solvent with the electrolyte causing reversible volume variations and device actuation. Consequently, they are very reliable Faradaic motors; the rate of the movement is a linear function of the reaction driving current and the amplitude of the bending movement is under linear control of the consumed charge.<sup>[11–14]</sup> In addition, the fabrication methodology is very robust; by using different devices (different shapes, including different masses of the CP and fabricated during sev-


eral years), the same actuation charge per unit of polymer mass always generates the same displacement.<sup>[11,13]</sup>


The exchange of ions is controlled by the driven electrochemical reactions. The exchange of solvent is driven by physical osmotic or electro-osmotic effect following, or driven by, respectively, the ionic exchange.<sup>[15–17]</sup> As a consequence of the delay between Faradaic and osmotic effects, the coulo-dynamic responses show some hysteresis; for the same charge, the muscle position during the forward (oxidation) and return (reduction) is different (actuation hysteresis cycle or dynamical hysteresis). In addition, some devices present creeping effects; after an oxidation/reduction cycle some devices do not recover the initial position.<sup>[18–27]</sup> Recently, irreversible reactions taking place in some CPs were identified as one of the creeping-effect origins (chemical creeping).<sup>[28]</sup>

By changing the solvent, some CPs move from a reaction-driven exchange of cations to reaction-driven exchange of anions.<sup>[29–31]</sup> By changing the salt (NaBr and NaCl) in aqueous solutions, the PPy–HpPS/tape (PPy–HpPS: polypyrrole–paraphenolsulfonic acid blend), the muscle moves from reaction-driven exchange of Br<sup>−</sup><sup>[32]</sup> to a consecutive exchange of cations (Na<sup>+</sup>) and anions (Cl<sup>−</sup>) in NaCl.<sup>[33]</sup> Those results should indicate that the muscle actuation, and the reaction-driven ionic exchange in CPs, is conditioned by the variation of the intra- and intermolecular forces inside the polymer under the influence of different physical or chemical variables. By changing the solvent or the salt, the dielectric constant, permittivity, dipolar moments, polymer-ion interactions, or salt dissociation degrees in both the dense polymer gel and the electrolyte should change, altering the ionic exchanges and the concomitant actuation mechanism.

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Herein, we present the attained results from a different salt, that is,  $\text{NaPF}_6$  aqueous solutions, in which the anion is closer to  $\text{Br}^-$  from a chemical point of view. A comparative study between an asymmetric bilayer muscle (comprised of two different CPs) and each of the two CP/tape bilayers muscles is presented.

## 2. Results and Discussion

### 2.1. Bilayer Muscles

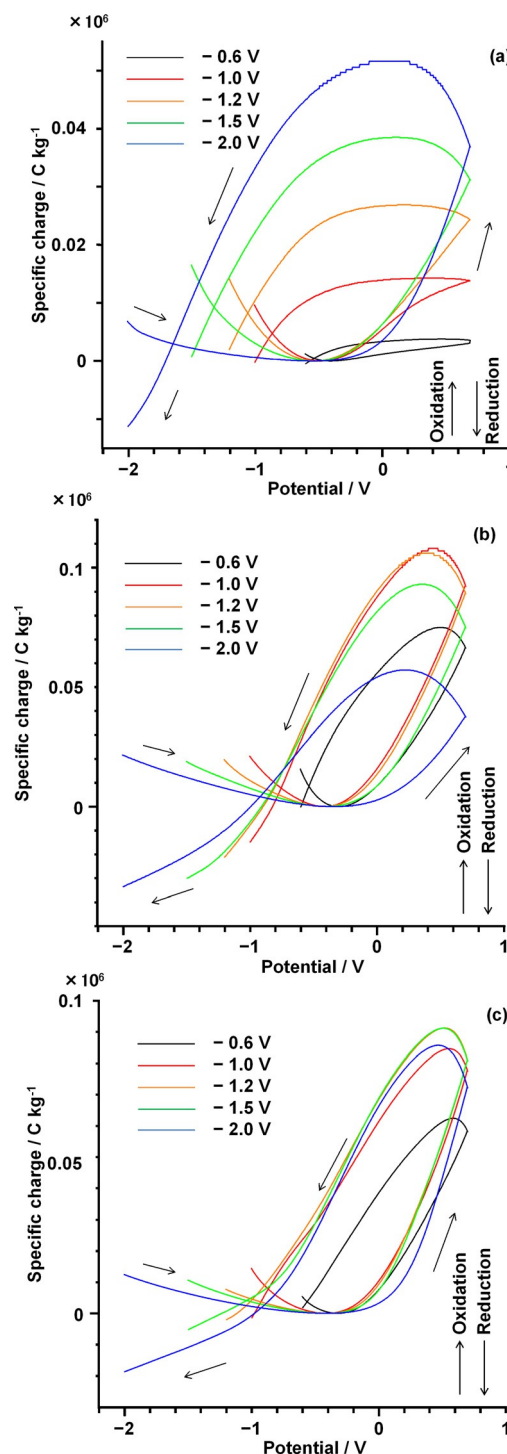
The three studied bilayer muscles are represented here as: tape/PPy-DBS, PPy-HpPS/tape, and PPy-HpPS/PPy-DBS, indicating the relative (left/right) position of each layer component during experiments. Thus, clockwise/anticlockwise bending movements will be attained under the following reaction-driven volume changes:

- 1) From the tape/PPy-DBS bilayer by PPy-DBS swelling/shrinking, respectively.
- 2) From the PPy-HpPS/tape bilayer by PPy-HpPS shrinking/swelling, respectively.
- 3) From the PPy-HpPS/PPy-DBS asymmetric bilayer by predominant PPy-HpPS shrinking or PPy-DBS swelling (clockwise) versus preponderant PPy-HpPS swelling or PPy-DBS shrinking (anticlockwise).

### 2.2. Influence of the Cathodic Potential Limit

Figures 1a–c show stationary coulo-voltammetric ( $Q/E$ ) responses (each closed loop minimum was taken as the charge zero origin) from the tape/PPy-DBS, PPy-HpPS/tape, and PPy-HpPS/PPy-DBS bilayer muscles, respectively, in 0.5 M  $\text{NaPF}_6$  aqueous solutions. We used the specific charge (charge consumed by reaction of the mass unit of CP working inside the electrolyte) because, for artificial muscles exchanging anions<sup>[11]</sup> or cations,<sup>[34]</sup> both the rate of the movement and the angular position are linear functions of the driving current or specific charge, respectively, and, therefore, independent of the film thickness or muscle dimensions. Each bilayer  $Q/E$  stationary response was obtained after consecutive cycles up to the same anodic potential limit of 0.7 V from a different cathodic potential limit, ranging between  $-0.6$  and  $-2.0$  V. Positive charge increases describe oxidations, whereas negative charge increases are related to reduction reactions.<sup>[35]</sup> Each  $Q/E$  response is comprised of two different parts: a closed coulo-voltammetric loop, for which the charge (maximum minus minimum) increase gives the charge consumed by reversible oxidation/reduction of the PPy films, and an open part on the left side, for which a charge increase from the initial potential of the cycle to the final potential is the charge consumed by irreversible and slow hydrogen evolution from the organic acid (HDBS or the HpPs) taking part in the CP.<sup>[36]</sup>

From the tape/PPy-DBS bilayer (Figure 1a), both reversible (closed loop) and irreversible (open part) charges increase for rising cathodic potential limits. The reversible charge increase



**Figure 1.** a) Coulo-voltammetric responses from PPy-DBS/tape bilayer artificial muscle in  $\text{NaPF}_6$  aqueous solutions obtained by increasing the cathodic potential limit (from  $-0.6$  to  $-2.0$  V) to the same anodic potential limit of 0.7 V. The same experiments were repeated for b) PPy-HpPS/tape muscle and c) PPy-HpPS/PPy-DBS muscle.

from 1 to 11 mC when the cathodic potential limit moves from  $-0.6$  to  $-2.0$  V, indicating that the polymer reduction occurs in the full studied potential range, up to high cathodic potential limits. Irrespective of the cathodic potential limit, most of the voltammetric charge is consumed by the reversible film oxidation and reduction reactions.<sup>[35]</sup>

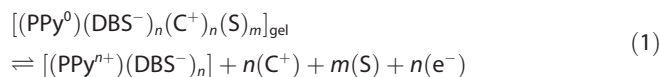
In terms of the  $Q/E$  response from the PPy–HpPS/tape bilayer muscles (Figure 1b), the charge of the closed loop (reversible charge) increases (from 4 to 6 mC) when the cathodic potential limit shifts from  $-0.6$  to  $-1.2$  V. Then, the reversible charge drops to 3 mC when the potential limit rises to  $-2.0$  V. The irreversible charge always increases with the cathodic potential limit.

The asymmetric bilayer shows (Figure 1c) an intermediate behavior; the redox activity of the bilayer increases from 10 to 13 mC and then drops to 12 mC when the cathodic potential limit moves from  $-0.6$  to  $-1.5$  and then to  $-2.0$  V, respectively. The irreversible charge increase is very fast when the cathodic potential limit moves from  $-1.5$  to  $-2$  V.

From the video frames recorded during the bilayers bending movement in parallel to the applied potential cycle, between  $-1.0$  and  $0.7$  V at  $10 \text{ mV s}^{-1}$ , the dynamo-voltammetric (angle-potential,  $\alpha/E$ ) plots were attained (Figure 2a from the tape/PPy–DBS bilayer, Figure 2b from the PPy–HpPS/tape bilayer, and Figure 2c from the PPy–HpPS/PPy–DBS asymmetric bilayer). The images in Figure 2d show the asymmetric bilayer muscle position at each potential point, as indicated on the  $Q/E$  response in Figure 2c, and the described angular displacement

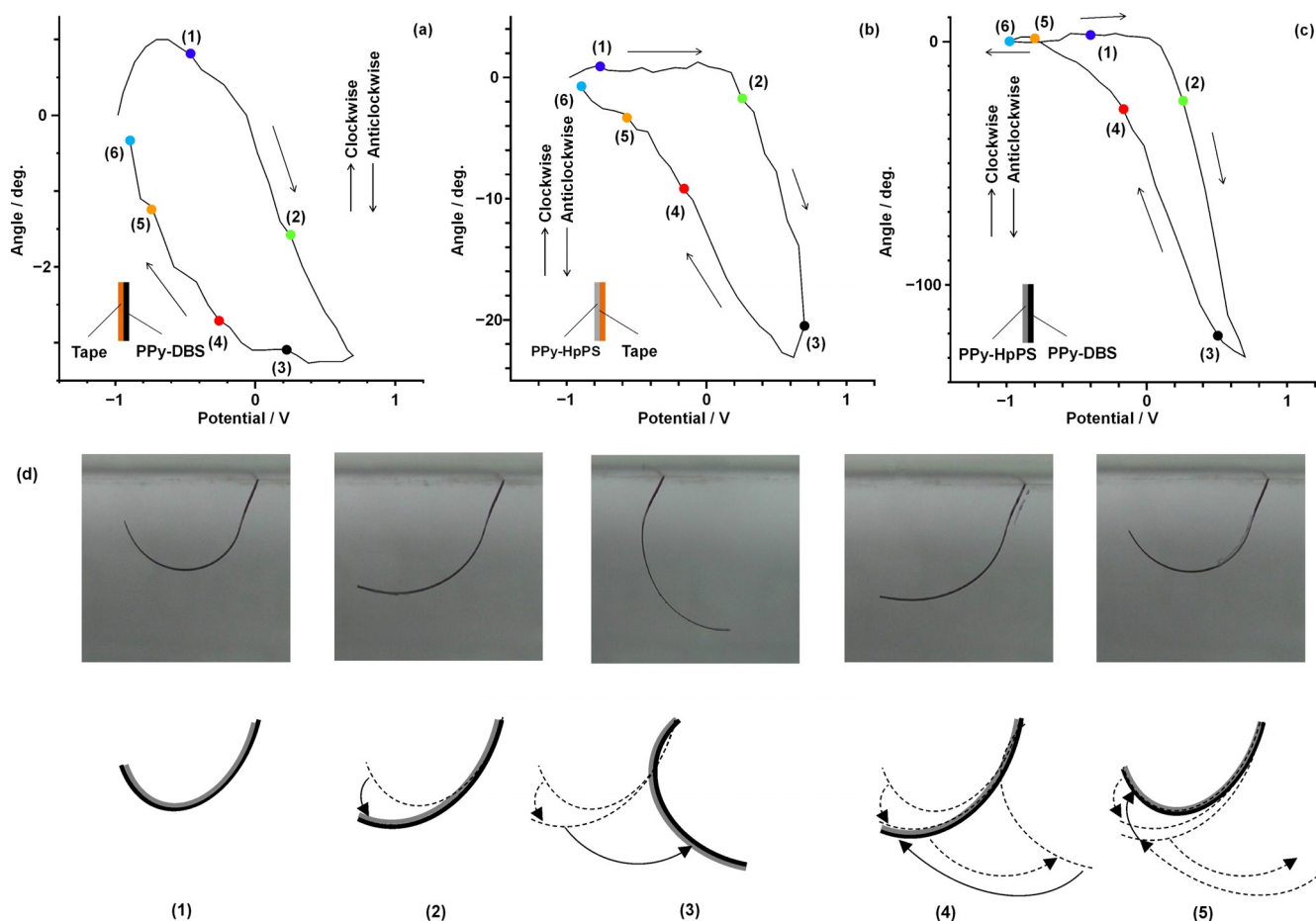
between the consecutive potential (points on the  $Q/E$  response).

The three muscles present a similar  $\alpha/E$  behavior, that is, an anticlockwise bending movement during oxidation and clockwise bending movement during reduction. This means that the PPy–DBS film from the tape/PPy–DBS bilayer shrinks during oxidation and swells during reduction; the electrochemical reaction drives the exchange of  $\text{Na}^+$  [Eq. (1)]:



where  $\text{PPy}^0$  represents the neutral PPy chains,  $\text{C}^+$  are the cations exchanged to keep the electroneutrality,  $\text{S}$  are solvent molecules to keep the osmotic pressure balance inside the polymeric gel (indicated by subindex gel), and  $\text{PPy}^{n+}$  represents every oxidized PPy chain after removal of  $n$  electrons ( $e^-$ ).<sup>[37]</sup>

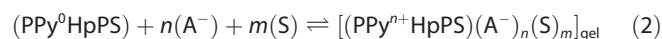
The amplitude of the described angle is only  $4^\circ$ . In a previous paper, an angle of  $50^\circ$  was attained in NaBr aqueous solutions under analogous potential cycling.<sup>[32]</sup> This indicates a strong in-



**Figure 2.** Evolution of the described angles from the different bilayer artificial muscles: a) PPy–HpPS/PPy–DBS, b) PPy–HpPS/tape, and c) PPy–DBS/tape artificial muscles in  $0.5 \text{ M NaPF}_6$  aqueous solution during voltammetric experiments between  $-1.0$  and  $0.7$  V at  $10 \text{ mV s}^{-1}$  at room temperature. d) Images of the PPy–HpPS/PPy–DBS artificial muscles in  $0.5 \text{ M NaPF}_6$  aqueous solution.

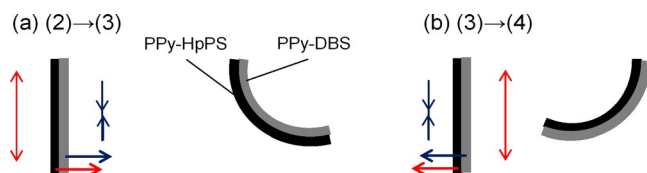
fluence of the anion, although, according with Equation (1), this influence could be neglected.

For the PPy–HpPS/tape bilayer, the oxidation-driven clockwise angular displacement means that the PPy–HpPS film swells during oxidation, shrinking during reduction to give anticlockwise movement. Therefore, the reversible electrochemical reaction drives the exchange of anions,  $A^-$ , ( $PF_6^-$  here) [Eq. (2)].<sup>[33]</sup>



Again, a strong influence of the anions emerges, when compared with the results attained from NaCl aqueous solutions, whereby cations were exchanged at the beginning of the anodic potential sweep and anions at the end of the sweep; for the results obtained from NaBr solutions, only the anion is exchanged in the full potential range. As a consequence, the amplitude of the angle described here per cycle was  $24^\circ$  and only  $14^\circ$  in the previous work (cation exchange followed by anion exchanges gives opposed bending movements during the anodic sweep).

As a partial conclusion, in  $NaPF_6$  aqueous solution during oxidation, the PPy–DBS film shrinks and the PPy–HpPS film swells. Reverse structural changes are produced in the two PPy-based materials upon reduction. Thus, when the asymmetric PPy–HpPS/PPy–DBS bilayer was checked in  $NaPF_6$  aqueous solution, both films developed a cooperative dynamic effect; when one of the layers swells and pushes the bending bilayer under oxidation, the second layer shrinks through oxidation and trails the muscle giving larger angular displacements. Structural changes and resulting forces reverse during the bilayer reduction (Figure 3). As a consequence of this coopera-



**Figure 3.** Scheme showing the cooperative actuation of the bending PPy–HpPS/PPy–DBS asymmetric bilayer muscle. Points (2) and (3) correlate with both the dynamo-voltammograms shown in Figure 2 and the coulo-dynamic evolution of the described angles shown in Figure 4.

tive actuation of the two constitutive layers, the angle described by the asymmetric bilayer per voltammetric cycle is  $133^\circ$ , which is more than six times the amplitude described per cycle for the PPy–HpPS/tape muscle ( $22^\circ$ ) and over 33 times that described by the tape/PPy–DBS muscle ( $4^\circ$ ) when cycling in the same potential range. A second consequence of the cooperative actuation of the two layers in  $NaPF_6$  is a very low creeping effect of  $0.3^\circ$  per cycle.

In conclusion, owing to the cooperative actuation, when both layers follow complementary volume changes (swelling/shrinking or shrinking/swelling) driven by the same electrochemical reaction, the angular displacement per potential

cycle is greater than those attained from each of the PPy–HpPS/tape or tape/PPy–DBS bilayer muscles.

### 2.3. Coulo-dynamic Evolutions in $NaPF_6$ Aqueous Solutions

By combining Figures 1 and 2, the evolution of each muscle position (angle) as a function of the specific consumed charge (coulo-dynamic evolution) in  $NaPF_6$  aqueous solutions is attained, as depicted in Figures 4a–c. The PPy–HpPS/PPy–DBS muscle angular displacement per cycle is  $133^\circ$  (Figure 4c), which is several times higher than those described by the PPy–HpPS/tape bilayer ( $22^\circ$  per cycle; Figure 4b) or by the PPy–DBS/tape bilayer ( $4^\circ$  per cycle; Figure 4a) in the same electrolyte. The coulo-dynamic efficiencies (slopes) result in 8.5, 3.0, and  $1.0^\circ mC^{-1}$  for the asymmetric bilayer, the PPy–HpPS/tape bilayer, and the PPy–DBS/tape bilayer, respectively. The magnitudes, described angle per cycle, and coulo-dynamic efficiency quantify the cooperative dynamical effect of the two layers in the asymmetric bilayer muscle.

Both anodic and cathodic displacements show a linear dependence on the charge, with a similar slope, corresponding to any Faradaic process driven by the reactions given in Equations (1) and (2). The charge spent at the beginning and at the end of the oxidation shows a very low efficiency toward bending the muscle. These charges can be related to hydrogen evolution from the film, producing acids, at the most cathodic potentials and to the elimination of protons at the most anodic potentials.<sup>[36,38]</sup> Both reactions result in very low volume variations.

In  $NaPF_6$  aqueous solution, all of the studied CP/tape bilayers behave as Faradaic motors; the amplitude of the described angle,  $\alpha$ , is a linear function of the consumed charge,  $Q$  [Eq. (3)]:

$$\alpha = \alpha_0 + kQ \quad (3)$$

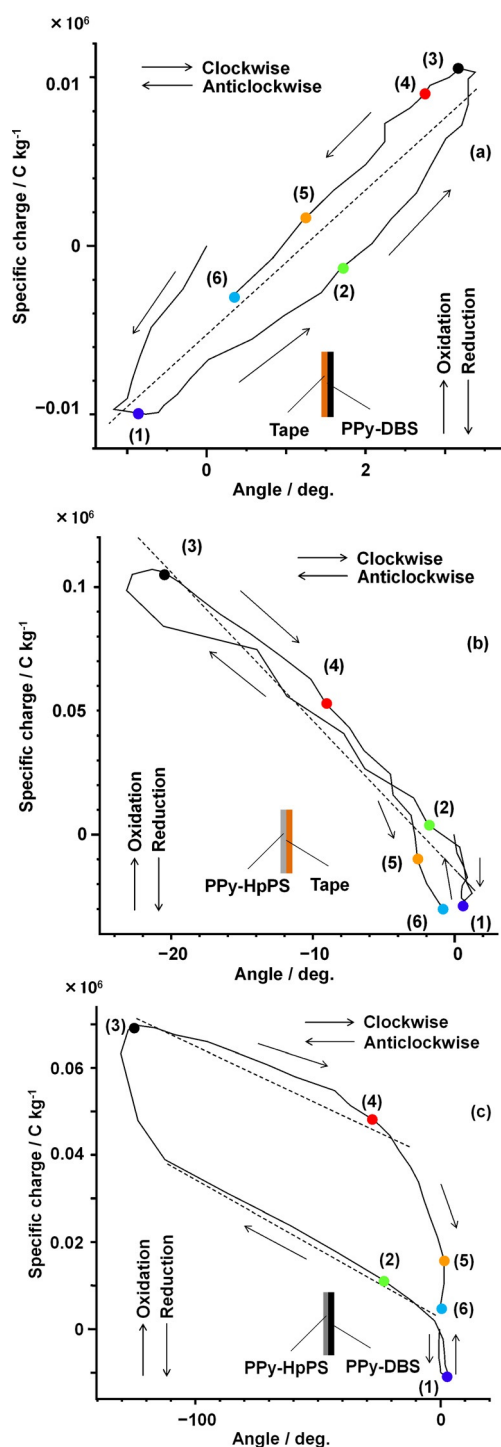
where  $\alpha_0$  is the initial angle and  $k$  ( $^\circ mC^{-1}$ ) is a constant dependent on the system (CP, electrolyte, tape, or second CP film).

Nevertheless, the actuation of the asymmetric bilayer presents an important hysteresis effect; for the same charge, the muscle positions during the anodic and the cathodic sweeps are quite different. Smaller hysteresis effects were attributed in previous systems to osmotic and electroosmotic physical effects.<sup>[33,39]</sup> Here, important fractions of the involved charge are consumed at the end of the anodic and cathodic sweeps, giving very low angular displacements (Figure 4c), pointing to an important contribution of the irreversible charge fractions detected in Figure (1) to the observed hysteresis.

The cooperative actuation in the asymmetric bilayer leads to a higher efficiency of the consumed charge describing larger angular displacements per unit of consumed charge, which is almost one order of magnitude higher than those described by each of the CP/tape bilayers.

Nevertheless, the use of CP blends including anions from large organic acids results in important hysteresis effects, which means complex control of the motor movement.





**Figure 4.** Relationship between the bending angle described for the muscles and the electrical charges consumed during voltammetric experiments studying reactions of different artificial muscles between  $-1.0$  and  $0.7$  V at  $10 \text{ mV s}^{-1}$  at room temperature: a) PPy-DBS/tape, b) PPy-HpPS/tape, and c) PPy-HpPS/PPy-DBS artificial muscles in  $\text{NaPF}_6$  aqueous solution.

In the two studied aqueous electrolytes ( $\text{NaCl}$  and  $\text{NaPF}_6$ ), the expansion and contraction of the PPy-HpPS film dominates the reaction-driven bending movement of the asymmetric bilayer. The PPy-DBS oxidation/reduction has a minor influence on the described amplitude of the angular displacement.

The resulting cooperative actuation, when both layers follow complementary volume changes (swelling/shrinking or shrinking/swelling) driven by the same reaction, leads to larger described angles per potential cycle than those attained from each of the PPy-HpPS/tape or tape/PPy-DBS bilayer muscles.

In addition to the electrochemical chemo-dynamic results, it is remarkable that, in  $\text{NaPF}_6$  aqueous solutions, the PPy-HpPS film exchanges, under oxidation/reduction,  $\text{PF}_6^-$  with the solution for charge balance. In a previous paper, the same bilayer muscle in  $\text{NaCl}$  aqueous solutions exchanged cations at the beginning of the oxidation sweep and anions at the end of the oxidation sweep. We can conclude that only by changing the anion of the dissolved salt ( $\text{NaCl}$  vs.  $\text{NaPF}_6$ ) in PPy-HpPS are both the electrochemical reaction and the driven ionic exchanges modified. This is equivalent to saying that the presence of  $\text{PF}_6^-$  in solution modifies, at least, the PPy-pPS, PPy- $\text{PF}_6^-$ , Na-pPS, and  $\text{PF}_6^-$ - $\text{Na}^+$  interaction forces inside the reacting film, moving from weak Na-pPS interactions to strong ones;  $\text{Na}^+$  balancing the pPS $^-$  anion is not expelled during oxidation, forcing the entrance of  $\text{PF}_6^-$ , which is required to balance the positive charges generated on the PPy chains [Eq (2)].

CPs have been considered, during their electrochemical reactions in liquid electrolytes, as the simplest material models of the intracellular matrix (ICM) dense gel of living cells.<sup>[40]</sup> Recently, it has also been discovered that by changing the solvent, but keeping the same dissolved salt, also changes the reaction-driven exchange of cations by exchange of anions.<sup>[29]</sup> These results show that CPs and bending artificial muscles constitute a good model for the study and quantification of intermolecular forces evolved during reactions in biomimetic reacting dense gels.

### 3. Conclusions

We have presented a comparative coulo-voltammetric ( $Q/E$ ), dynamo-voltammetric ( $\alpha/E$ ), and coulo-dynamic ( $Q/\alpha$ ) study in  $\text{NaPF}_6$  aqueous solution of the asymmetric polypyrrole bilayer muscle (PPy-HpPS/PPy-DBS) and the two bilayer muscles tape/PPy-HpPS and PPy-DBS/tape.

The  $Q/\alpha$  responses indicate that, in the tape/PPy-HpPS bilayer muscle, the actuation originates from reaction-driven exchange anions ( $\text{PF}_6^-$ ), swelling upon oxidation and shrinking upon reduction.

The PPy-DBS/tape bilayer actuation in  $\text{NaPF}_6$  aqueous solution drives the exchange of the cation ( $\text{Na}^+$ ), shrinking upon oxidation and swelling upon reduction.

Those opposed reaction-driven volume variations originate in the PPy-HpPS/PPy-DBS asymmetric bilayer muscle, with a cooperative actuation (dynamic synergy) increasing the angle described per unit of charge.

High cooperative actuation effects allow the development of more efficient polymeric motors for different medical tools or for the development of zoomorphic and anthropomorphic soft robots. In addition the cooperative actuation, it gives very low creeping effects.

The use of polymeric blends with organic anions or organic salts leads to large hysteresis actuating effects in aqueous solu-

tions; for the same charge, the muscles position is different during the anodic potential sweep compared to that during the cathodic sweep.

The presence of hysteresis effects during actuation results in complex control of the motor movement.

New families of CPs<sup>[13,37,41,42]</sup> must be explored to find the most important cooperative actuations in the absence of these important hysteresis effects, with minimum creeping effects.

## Experimental Section

Reactants, equipment, used electrochemical methodologies, electrogeneration of the CP monolayer and bilayer films, as well as the construction of the CP/tape bilayers were described in previous papers.<sup>[32,33]</sup>

PPy-DBS films were cut into 20 mm×1 mm strips, each one was 20 μm thick and had a mass of 0.5320±10 mg. A paint (Max Effect, Maxfactor) strip, 6.0–12.0 mm from the upper border, prevents direct contact between the electrolyte (by capillarity) and the metallic clamp that allows the electrical contact.<sup>[32,33]</sup> The PPy-DBS/tape bilayer muscle inside the solutions was 8 mm long. PPy-HpPS films were also cut into 20 mm×1 mm strips, each one was 20 μm thick and had a mass of 0.1370±15 mg. PPy-HpPS/PPy-DBS bilayer films were cut into 15 mm×1 mm strips and were 20 μm thick and had a mass of 0.3493 mg. Each film was painted with a transversal paint strip on both film sides, 2.0–7.0 mm of the upper border.

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**Keywords:** asymmetric bilayer muscles • conducting polymers • cooperative actuation • creeping • hysteresis

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