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Synthesis of light-driven motorized nanocars for linear trajectories and their detailed NMR structural determination

Víctor García-López [a, b], Lawrence B. Alemany [a, d, **], Pinn-Tsong Chiang [a], Jiuzhi Sun [a], Pin-Lei Chu [a], Angel A. Martí [a, c], James M. Tour [a, b, c, *]

[a] Department of Chemistry, Rice University, Houston, TX, 77005, USA
[b] Smalley-Curl Institute and NanoCarbon Center, Rice University, Houston, TX, 77005, USA
[c] Department of Materials Science and NanoEngineering, Rice University, Houston, TX, 77005, USA
[d] Shared Equipment Authority, Rice University, Houston, TX, 77005, USA

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ABSTRACT

The design and synthesis of a fluorescent light-driven motorized nanocar with a linear geometry is described. Due to its structural design, the nanocar is present as a mixture of two photo-interconvertible diastereomers. An extensive and detailed NMR study allowed the full assignment of the chemical shifts of the two diastereomers in the mixture. The nanocar is expected to translate in a linear motion due to the light-driven motor providing a paddle-wheel like propulsion. The quantum yield of 0.56 and the photostability of the dye make this nanocar suitable for future single-molecule fluorescence microscopy studies.

1. Introduction

Nanocars are synthetic molecular machines whose molecular components are comprised of a chassis, axles, wheels, and/or a motor. These molecular machines are designed to convert external energy into mechanical force and further generate controllable translational motion on surfaces.[1] Over the last decade, our group has synthesized a diverse series of nanocars to study the interaction between the nanocar's wheels and the surface,[2–5] to investigate different mechanisms of propulsion,[6–8] and to establish reliable methodologies for the tracking on surfaces.[9–11] Scanning tunneling microscopy (STM)[1,11] and single-molecule fluorescence microscopy (SMFM)[9,10] are the two main techniques used to track the nanocars, and both indicated that our nanocars translate on surfaces through a rolling mechanism and not through a stick-slip or sliding translation.[1,3,10] However, despite the success of previous nanocars, their motion was mostly driven by random thermal energy.

Feringa and co-workers developed a nanocar with four motorized wheels that perform translational motion on a Cu(111) surface at low temperatures. The rotation of the motors and therefore the translation of the nanocar was induced by tunneling electrons from the STM tip.[12] However, in the case of our nanocars, many single molecules should be triggered in parallel by a remote external stimulus. It was only recently that our group developed the first motorized nanocar that translates on conductive metallic surfaces upon remote photo-activation of a rotary motor as imaged by the Grill group.[13]

Our current efforts are directed to develop nanocars that can operate on non-conductive surfaces at ambient conditions (room temperature and exposed to air)[10,14] by converting light into controllable motion. Recently, we reported the synthesis of the first nanocar designed to operate at ambient conditions, which includes a light-driven motor to provide the propulsion, two BODIPY dyes in the axles for the tracking by SMFM, and four adamantane wheels (nanocar **1**, Fig. 1).[15] The BODIPY dye is part of the axle so as to avoid that moiety acting as an anchor to the surface, slowing the translation, as was demonstrated with a previous motorless fluorescent nanocar.[4]

* Corresponding author. Department of Chemistry, Rice University, Houston, TX, 77005, USA.
** Corresponding author. Department of Chemistry, Rice University, Houston, TX, 77005, USA.
E-mail addresses: lalemany@rice.edu (L.B. Alemany), tour@rice.edu (J.M. Tour).

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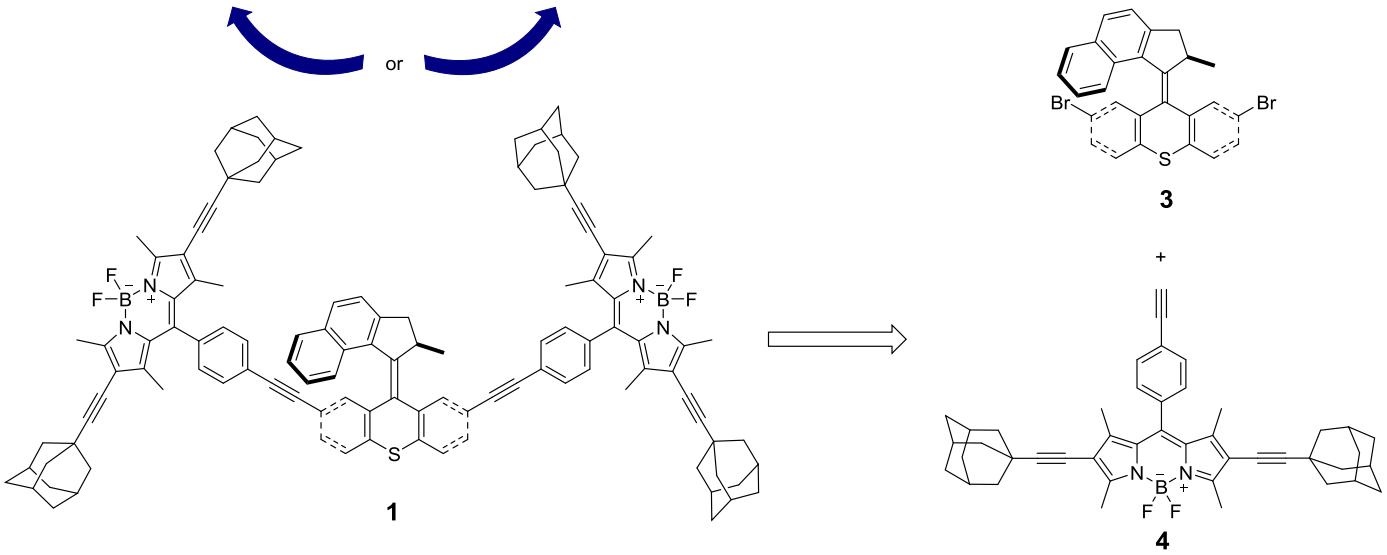

Fig. 1. Structure and retrosynthetic plan of fluorescent motorized nanocar **1**. Blue arrows show the expected direction of the trajectories.

Due to its angled chassis, nanocar **1** is expected to translate short distances in a semi-circular motion. For the nanocar to translate relatively long distances and in a linear trajectory, it must have a linear geometry; therefore, we designed nanocar **2** that has the axles in a parallel configuration (Fig. 2). Both nanocars are expected to move in either direction depending on the chirality of the motor and how they land on the surface.

The synthetic challenge of nanocar **2** is to construct a molecular motor functionalized with the axles in the 2,6-positions of the stator (motor **13**). This asymmetric motor would be made as two geometrical isomers because *trans*-**13** and *cis*-**13** are synthesized in one pot, and the two forms are interconvertible in the presence of

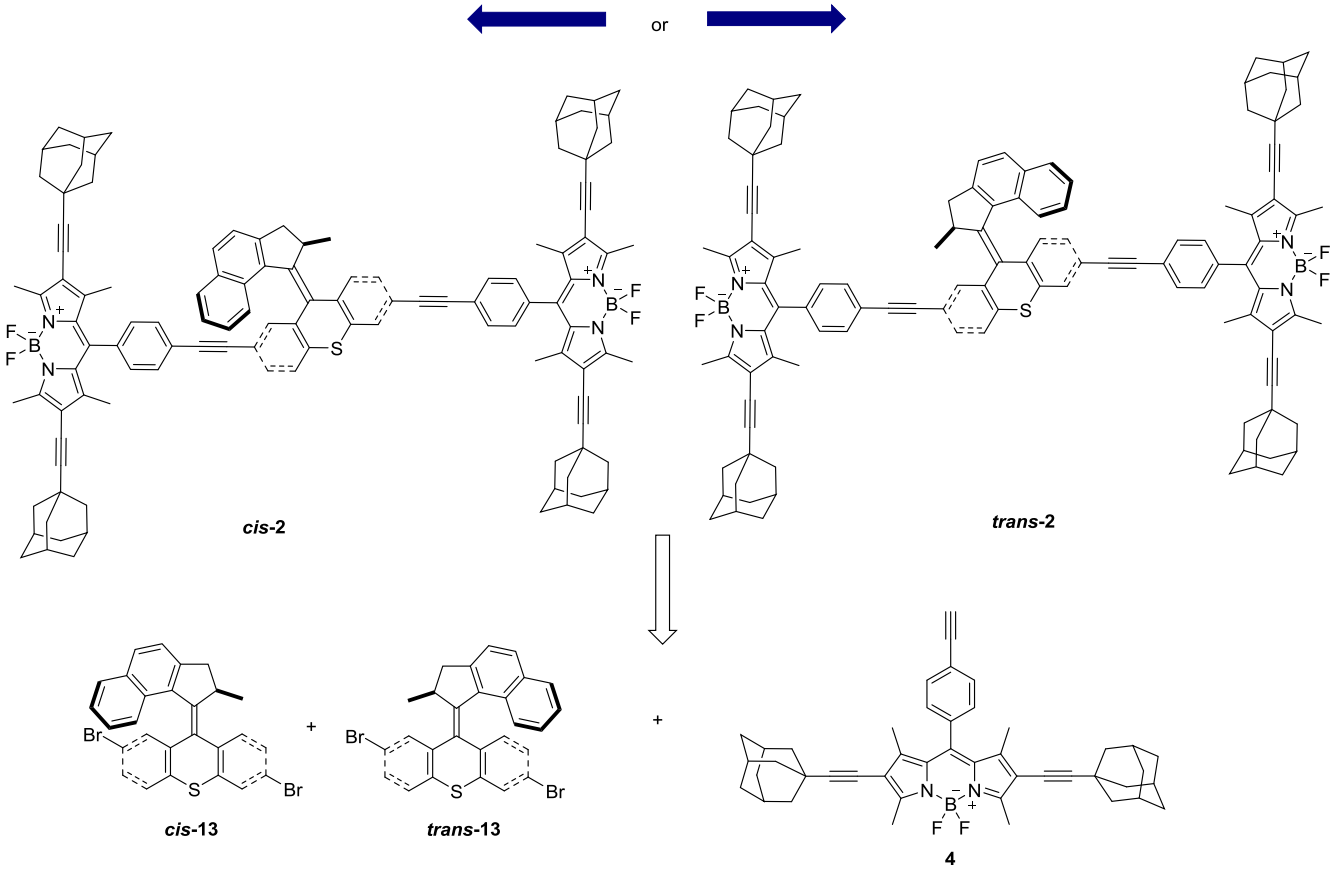

Fig. 2. Structure and retrosynthetic plan of fluorescent motorized nanocar **2.** Blue arrows show the expected direction of the trajectories.