Electronic Supplementary Material (ESI) for Chemical Communications

An acido-triggered reversible luminescent and nonlinear optical switch based on a substituted styrylpyridine: EFISH measurements as an unusual method to reveal a protonation/deprotonation NLO contrast

Electronic supplementary information

1. General and materials

Diphenyl-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenyl)-amine (DPVPA) was prepared by a slightly modified version of the procedure reported in the literature.[1] All reagents and catalysts were purchased from Sigma-Aldrich and used as received. Toluene was distilled over Na/benzophenone. Characterization was performed by ^{1}H and ^{13}C NMR (Bruker Avance DRX 400 spectrometer) and it is consistent with published data[1a]. Thin films were prepared by spin-coating on glass slides a solution prepared dissolving 12 mg of DPVPA (3.2 wt%) and 377 mg of PMMA (10 wt%) in 3 mL of $CHCl_3$:MeOH = 2:1(v/v).

Electronic absorption spectra were obtained using a Jasco V-530 spectrophotometer. Photoluminescence (PL) measurements were obtained by a Jobin-Yvon Fluorolog-3 spectrometer equipped with double monochromators and Hamamatsu-928 photomultiplier tube (PMT) as the detector.

2.1 Synthesis (E)-4-(4-bromostyryl)-N,N-diphenylaniline

To a solution of diethyl 4-bromobenzylphosphonate[2] (364 mg, 1.2 mmol, 1.1 equiv.) and 4-(diphenylamino)benzaldehyde (295 mg, 1.08 mmol, 1 equiv.) in THF (9 mL), under nitrogen, and cooled to 0 ºC was added, in small portions, potassium *tert*-butoxide (316 mg, 2.8 mmol, 2.6 equiv.). The cool bath was then removed and the mixture stirred for 18h at room temperature. After hydrolysis with water, the mixture was stirred for further 30 min. The reaction mixture was diluted with AcOEt and washed with water: the organic layer was dried over Na_2SO_4 and concentrated. The

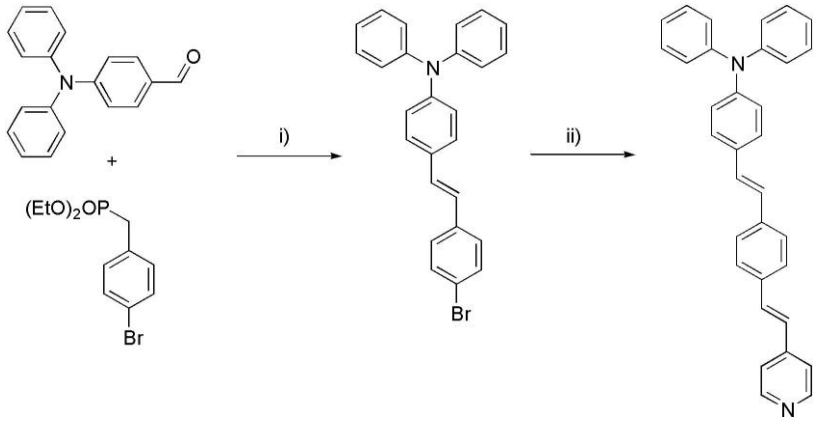
crude product obtained was purified by flash chromatography, using hexane/dichloromethane 1:1 as eluant, to give the product as a pale yellow solid (378 mg; yield 85%).

2.2 Synthesis of diphenyl-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenyl)-amine (DPVPA)

DPVPA was prepared according to Scheme 1 by Heck coupling of (E)-4-(4-bromostyryl)-N,N-diphenylaniline (160 mg, 0.37 mmol) with 4-vinylpyridine (75 μL, 0.695 mmol) in the presence of Pd[P(*t*-Bu)$_3$]$_2$ as catalyst in toluene at 80 °C for 60 hours under N_2 atmosphere. The reaction mixture was dried in vacuum and purified by chromatography on silica gel (hexane:AcOEt = 6:4) to give an orange solid (150 mg, 0.33 mmol, 90% yield).

NMR data (9.4 T, $CDCl_3$, 298 K, δ, ppm): ^{1}H NMR 8.59 (d, *J* = 6.0 Hz, 2H), 7.54 (s, 4H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 6.0 Hz, 2H), 7.30 (m, 4H), 7.14 (d, *J* = 7.5 Hz, 4H), 7.11(s, 1H), 7.07 (m, 4H), 7.04 (s, 1H), 7.02 (s, 1H), 7.00 (s, 1H); **^{13}C NMR** 150.21, 147.61, 147.47, 144.66, 138.23, 135.05, 132.78, 131.17, 129.31, 128.86, 127.46, 127.40, 126.71, 126.23, 125.52, 124.61, 123.39, 123.16, 120.79.

Scheme 1



i) *t*-BuO$^-$K$^+$, THF, RT, 16h, 85%; ii) Vinylpyridine/Pd[P(*t*-Bu)$_3$]$_2$/toluene, 80°C, 60h, 90%.

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[2] E. Diez-Barra, J. C. Garcìa-Martìnez , S. Merino, R. del Rey, J. Rodrìguez-Lòpez, P. Sànchez-Verdù, J. Tejeda, *J. Org. Chem.* 2001, **66**, 5664.