Novel fluorinated amino-stilbenes and their solid-state photodimerization†

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We synthesized a series of polyfluoro-amino-stilbenes in satisfactory yields by Wittig reaction of 4-piperazinyl-benzalhehydes with pentafluoro-benzylidene-triphenyl-phosphorane and we analyzed the photochemical behavior of these stilbenes in the solid state; thanks to arene–perfluoroarene π–π interactions, some of them have shown a good propensity to give the corresponding cyclobutane photodimers in quantitative yields. The photocyclization is reversible both in solution and in polymeric matrix, affording the corresponding stilbenes with different *cis–trans* stereo-selectivity.

Introduction

The photochemical transformations of organic molecules in the solid state are known since the end of the 19th century.[1] Among these, the photochemical [2 + 2] reactions of olefins, affording the corresponding cyclobutanes, have been extensively investigated and today their mechanisms are well known. To observe [2 + 2] photoreactions of olefins it is necessary to have double bonds parallelly arranged and with a distance between them in the 3.5–4.2 Å range.[2] More recently, such reactions have been exploited in materials science to produce new photoresists[3] or for the development of new solid-state optical memories for high capacity storage.[4] From the stereochemical point of view, in solution the photocyclization of olefins results in a mixture of stereoisomeric cyclobutanes. This is further complicated by photochemical *cis* ↔ *trans* isomerization occurring in solution, which produces a mixture of reacting *cis* and *trans* stereoisomers, increasing the number of possible stereoisomers. As an example, the [2 + 2] photocyclization of 2-butene produces 4 diastereoisomeric cyclobutanes,[5] but the situation is even more complicated when asymmetric olefins are reacting. A stereoselective photochemical [2 + 2] cycloaddition can be performed in the solid state, where intermolecular interactions are responsible for the correct arrangement of olefins.[6] In this case the stereochemistry of the products is determined by the crystal packing of the molecules and therefore these reactions are potentially very important for the synthesis of molecules with well-defined stereochemistry (topochemical reaction). Arene–arene interactions play a fundamental role in molecular recognition events, both in solution and in the solid state and their importance has been recognized in many areas, spanning from biology to materials science.[7] From this latter point of view, arene–perfluoroarene π–π interactions have gained interest as new supramolecular synthons and have been exploited to promote stereoselective topochemical reactions in the solid state. For instance single crystals of 2,3,4,5,6-pentafluoro-stilbene have been irradiated to give the corresponding cyclobutane (a single diasteroisomer) with high yield.[8,9] In this case, the arene–perfluoroarene interactions control the alignment and the distance between the two reacting double bonds. Indeed, diffraction analysis pointed out that olefinic double bonds are parallel arranged with an average distance of 3.704 Å, falling in the 3.5–4.2 Å range, therefore satisfying both the requisites to observe a topochemical [2 + 2] photocyclization reaction.[2]

Results and discussion

Few years ago, some of the authors prepared a series of stilbenes bearing a pentafluoro-phenyl group; these systems can work as "Push–Pull" systems[10] for non-linear optics applications (Scheme 1).

These molecules are structurally similar to the systems studied by Coates *et al.*, but the presence of dimethyl- or diphenyl-amino groups makes the non-fluorinated aromatic ring more electron-rich, and therefore it should enhance arene–perfluoroarene interactions in the solid state, thus facilitating the [2 + 2] photodimerization reaction. Starting from this background, we planned both to study the photoreactivity of molecules **1** and **2** and a series of new 2,3,4,5-pentafluoro-4′-dialkylamino-stilbenes in order to investigate their behavior in [2 + 2] photochemical reactions. In detail, we planned the synthesis of new fluorinated amino-stilbenes, in order to test the effect on the photoreactivity of bulkier substituents (such as piperazine) and also to access more complex systems, such as bis-stilbenes or photoreactive polymers. Such systems are the starting point for new and more complex systems, such as

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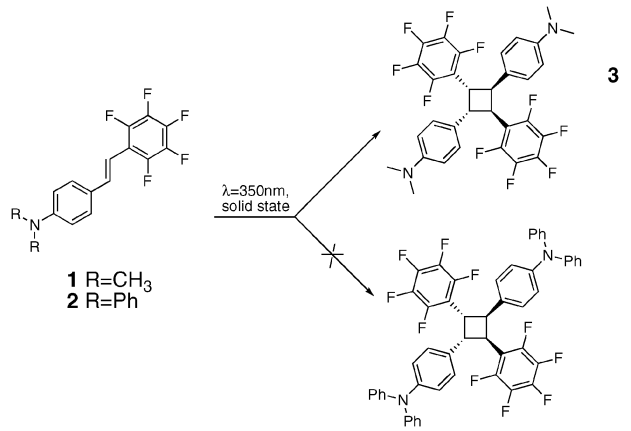
† Electronic supplementary information (ESI) available: Copies of ^{1}H, ^{13}C ^{19}F NMR spectra, copies of IR spectra of PMMA doped with **6b** and **18b**. CCDC 717576. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00264j



Scheme 1 General structure of 2,3,4,5-pentafluoro-4′-amino-stilbenes **1** and **2** (left) and their photodimerization in the solid state.

photo-polymerizable crystals and new cross-linkable polymers. We prepared 2,3,4,5-pentafluoro-4′-amino-stilbenes **1** and **2** by Wittig reaction between a *p*-dialkyl-amino-benzaldehyde and (2,3,4,5,6-pentafluoro-benzylidene)-triphenyl-phosphorane, following the procedure reported in the literature.[10] We obtained polycrystalline powders of **1** and **2** by crystallization from ethanol solution, but in the case of **1** we were able to grow single crystals suitable for X-ray diffraction by slow evaporation of ethanol solution. On the other side, in spite of the large number of trials, all the attempts to grow single crystals of **3** and of all the other compounds presented in this paper, suitable for X-ray diffraction, were unsuccessful. The crystal structure of **1**, determined by means of single crystal X-ray analysis, evidences nearly flat molecules (dihedral angle between phenyl and pentafluoro-phenyl group 4.5°) with a *trans* arrangement of the phenyl and pentafluoro-phenyl groups, in general referred as *HT* (*Head-to-Tail*) *anti* stereoisomer. Molecules of **1** are stacked in columns parallel to [001] with a head-to-tail arrangement dictated by perfluoroarene–arene interactions (Fig. 1). According to the classification proposed by Schmidt[11] crystal packing of **1** is of the α-type with adjacent molecular planes *ca.* 3.5 Å apart. This feature in the crystal structure of **1** is closely related to that of *trans*-pentafluoro-stilbene[8a] for which the *p*-dimethyl-amino unit is missing. Along the [001] columns there are two symmetry independent stacking interactions with distances between centroids of ethylenic moieties of 3.693 and 3.726 Å (Table 1, Fig. 1).

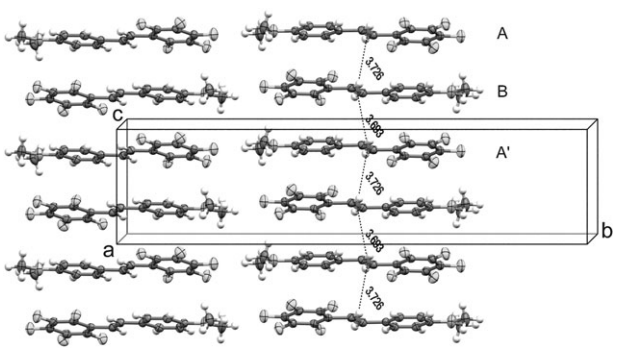


Fig. 1 Crystal packing of **1** showing the distances between ethylenic moieties of stacked molecules.

Table 1 Geometrical parameters for crystal of **1**

	A–B	B–C
θ	0.0°	0.0°
θ_2	97.5°	108.9°
θ_3	69.4°	87.8°
d	3.726 Å	3.693 Å
D_1	0.5 Å	1.22 Å
D_2	1.30 Å	0.13 Å

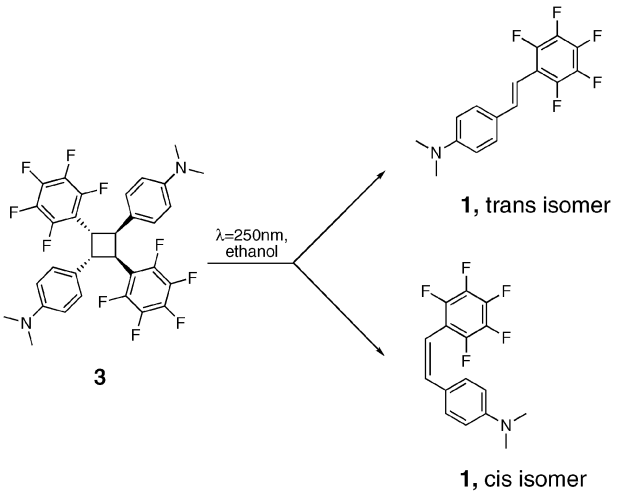
The two crystallographically independent stacking interactions along [001], described by the geometrical parameters θ_1, θ_2, θ_3, D_1 and D_2 (Table. 1),[12] are in accordance with the highly efficient photodimerization, *i.e.* the relative arrangement of adjacent reacting ethylenic moieties is quite favorable. Indeed, photocyclization of **1** occurs under very mild irradiation conditions and results in a quantitative yield for product **3** (Scheme 1). The stereochemistry of cyclobutane **3** on the basis of ^{1}H NMR data, the crystal structure of the parent molecule **1** and the topochemical rules for solid-state photoreactions should correspond to the *anti* head-to-tail coupling of two 2,3,4,5,6-pentafluoro-4′-dimethylamino-stilbene molecules. In fact, the ^{1}H NMR spectrum of cyclobutane shows only a broad resonance for the hydrogen atoms, centered on 4.5 ppm; this result proves that only one stereoisomer is present. On the basis of the middle point method proposed by Ben-Efraim and Green[13] and according to the data reported by Coates *et al.* for cyclobutanes obtained from the photodimerization of crystals of pentafluoro-stilbene,[8a] the stereoisomer of **3** formed in this reaction is that reported in Scheme 1, that is the HT *anti* stereoisomer. The quantitative yield obtained for **1** is unusual among photodimerization reactions, which normally are less than 100% since the produced photodimers tend to isolate the reactive molecules in the crystal matrix (for evenly spaced olefin stacks the theoretical maximum yield is 86.5%).[14] The different steric requirements for the parent and product molecules often reduce the ability of the former to accommodate product molecules as a stable solid solution quite early during reaction. In general, the photoproduct can hardly be a substitutional solute with significant concentration in the parent crystal due to its high steric crowding. In **1**, the arrangement of C=C bonds makes crystals highly reactive in photodimerization even with a very low power light source (*e.g.* the light source of an optical microscope set at minimum power). Within few minutes from the beginning of irradiation, the crystals start to bend and crack under the mechanical lattice strain promoted by photodimerization to the bulkier cyclobutane derivative **3**, eventually exploding. Observation under the optical microscope revealed that the crystals crack parallel to the {001} plane.

Compound **1** absorbs at 350 nm (the wavelength which promotes the [2+2] cyclodimerization), while **3** is completely transparent at this wavelength. When using a halogen lamp, at the beginning the photodimerization of **1** occurs close to the surface of the crystal, because the crystal is not completely transparent at this wavelength and therefore the inner part of the crystal cannot react. Later, during the photoreaction, because the external layer formed by photocyclization is transparent, the radiation can reach also the inner part of

the crystals, promoting the photoreaction. This feature together with the favorable crystal packing is responsible for the high conversion yield observed for this compound. Since the photodimerization starts close to the surface, in order to study its reactivity, we analyzed the surface topography of a (010) crystal face under irradiation with an optical fiber lamp by atomic force microscopy (AFM). During the early stages of the photoreaction small holes on the terraces were observed with concomitant appearance of spheroidal features, which grew at the expenses of the surface material (Fig. 2a, b, g and h). On continuing irradiation of the crystal, more dramatic changes occurred, eventually leading to the formation of a new crystalline phase on top of the reacting crystal, showing no azimuthal orientation relative to the surface of the parent crystal (Fig. 2c–e). Possible eroding effects due to the scanning tip could be ruled out by observing that microcrystals of the new phase grew even larger outside the scanned area (Fig. 2f). The presence of the spheroids can be related to the enthalpy released during the conversion of two C=C bonds to four C–C bonds of a cyclobutane ring causing the formation of product molecules in an initial amorphous phase (ΔH_0 for gas phase reaction of two molecules of ethylene to afford one molecule of cyclobutane = −77.1 kJ mol^{-1} [15]) and showing a high molecular mobility which allows post-crystallization in a few minutes.

While compound **1** underwent photodimerization in the solid state affording quantitatively the corresponding cyclobutane derivative **3**, we did not observe any photocyclization for compound **2**. We attribute the lack of reactivity in the solid state to the steric hindrance of the phenyl groups, which keep the stilbene cores separated, thus hindering the double bonds from getting close enough to react.

The [2 + 2]-photodimerization of olefins is, in principle, a reversible reaction under photochemical conditions. Preliminary studies have shown that our photodimerization reaction is



Scheme 2 Photostimulated retrocyclization of **3** in ethanol solution.

reversible; irradiation of an ethanol solution of **3** with λ_{exc} = 254 nm results in a mixture of *cis* and *trans* isomers of **1**. These isomers arise from the two possible retrocyclization pathways: the first (path a) yielding the starting *trans*-stilbene **1** and the second one (path b) affording the *cis* isomer (Scheme 2). A useful feature emerging from this preliminary study is that **1** and **3**, having different absorption maxima, exhibit both photodimerization and retrocyclization at different wavelengths (λ > 350 or λ = 254 nm). Moreover, compound **1** is also highly fluorescent, even in the solid state, while compound **3** is not fluorescent.

Starting from these interesting results, we planned and carried out the synthesis of new stilbene derivatives, starting from *p*-fluoro-benzaldehyde, which was allowed to react in DMSO with *N*-methyl- or *N*-BOC-piperazine in the presence of K_2CO_3 at 100 °C, affording 4-piperazinyl-aldehydes **4a,b**.

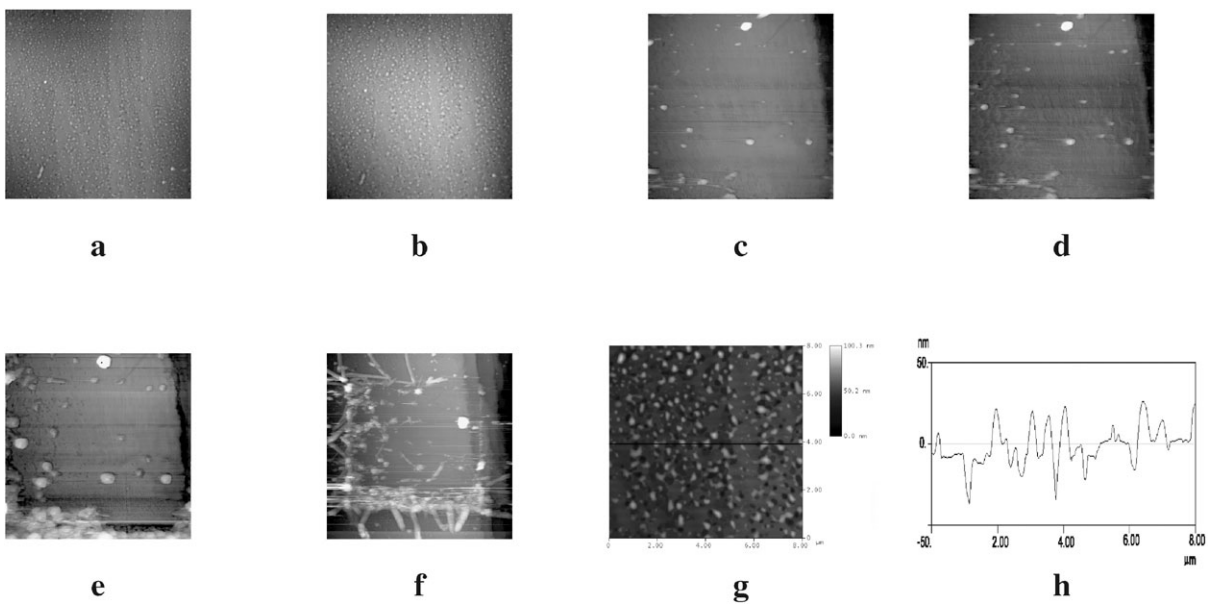
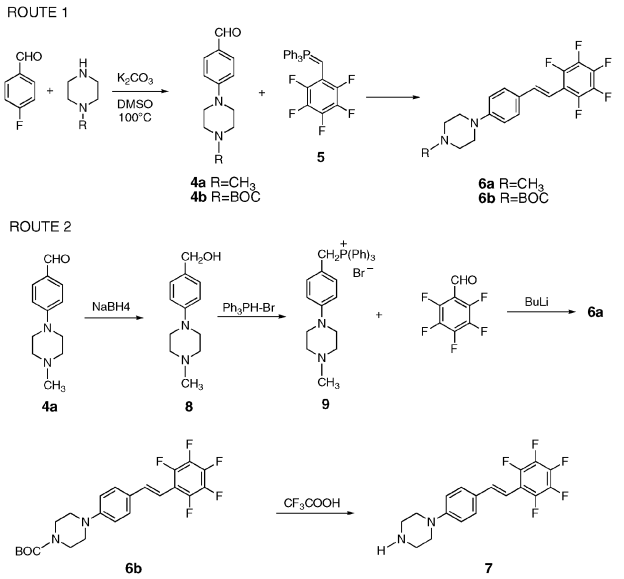


Fig. 2 **1** → **3** Transformation observed with the AFM (scan size: a–b 20 μm; c–e 30 μm; f 45 μm. Elapsed time: 5 minutes between subsequent images); g: zoom of frame b showing etch pits arising from the reaction of crystal surface of **1** to produce an amorphous phase of **3**; h: cross-section profile through the black line in g showing height and deepness of drop-like features and etch pits, respectively.

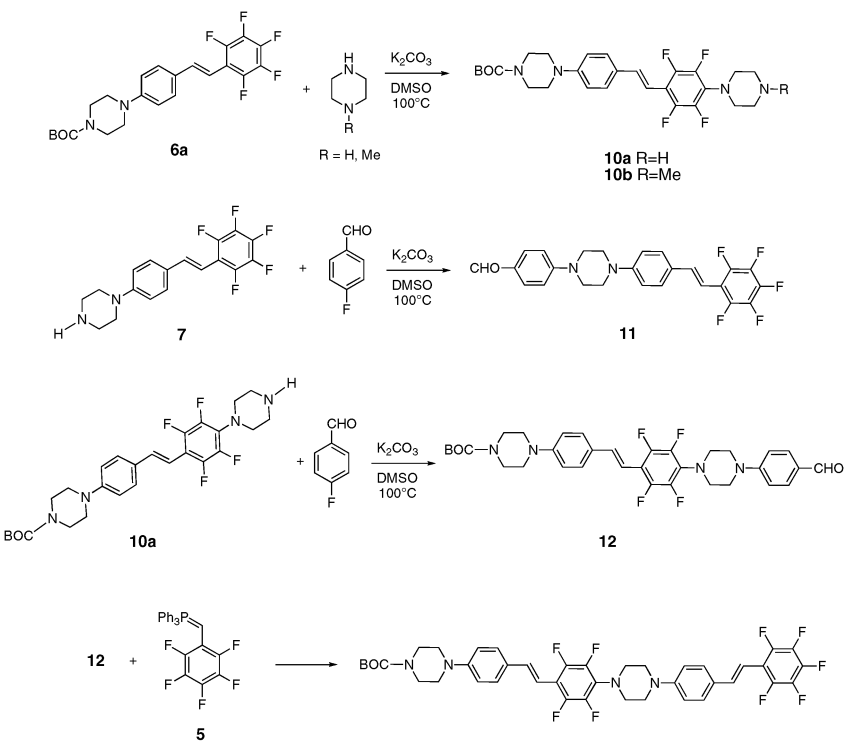


Scheme 3 Synthesis of piperazinyl-based pentafluoro stilbenes.

We transformed the aldehydes **4**, through Wittig reactions with the pentafluoro-benzylidene-phosphorane **5**, into the corresponding *trans* pentafluoro-stilbenes **6a,b**, collected, respectively, in 60 and 71% yields. Treatment of **6b** with trifluoro-acetic acid afforded the corresponding piperazine derivative **7** in 90% yield. The synthetic procedure is summarized in Scheme 3. Compound **6a** was prepared also following an alternative procedure. *p*-(4-Methyl-piperazinyl)-benzyl alcohol (**8**) (prepared by reduction of the corresponding aldehyde **4a** with $NaBH_4$) was reacted with triphenyl-phosphonium bromide ($HPPh_3Br$), affording the corresponding phosphonium salt (**9**). This latter compound was then transformed into the corresponding phosphorane, by treatment with BuLi. The reaction of the phosphorane with pentafluoro-benzaldehyde afforded the desired compound **6a**. Both benzyl alcohol **8** and triphenyl-phosphonium bromide **9** have been never described so far in the literature.

We investigated stilbenes **6a** and **6b** as starting materials to access more functionalized substrates. In particular, we tested the nucleofugacity of fluorine atoms of pentafluoro-phenyl rings in nucleophilic aromatic substitution reactions with piperazine or *N*-methyl-piperazine. As expected, under the same conditions used in the preparation of compounds **4a–b**, we obtained the *p*-tetrafluoro substituted piperazine derivatives **10a** and **10b** in 63 and 29% yield, respectively. Both the derivatives **7** and **10a** react as nucleophiles with *p*-fluoro-benzaldehyde affording the corresponding products of *N*-arylation **11** and **12**. The most ambitious target of this strategy has been the synthesis of bis-stilbenes. Stilbene **12** was reacted with pentafluoro-benzylidene-phosphorane **5**, affording the desired, head-to-tail, bis-stilbene **13** (Scheme 4).

A similar approach was applied to prepare the analogous head-to-head bis-stilbene. Stilbene **11** was reacted with the phosphorane **5** under standard Wittig conditions but the formyl-phenyl derivative was found totally unreactive. In order to prepare this product, we explored also an alternative route. *N*,*N*′-Bis(*p*-formyl-phenyl)-piperazine **14** was prepared as described in the literature starting from *p*-fluoro-benzaldehyde and piperazine in the presence of K_2CO_3 and then reduced to the corresponding alcohol **15** by $NaBH_4$. Alcohol **15** was then transformed in one step into the corresponding phosphonium salt **16** by reaction with $HPPh_3Br$. Compound **16** was treated with BuLi to prepare the corresponding phosphorane and then

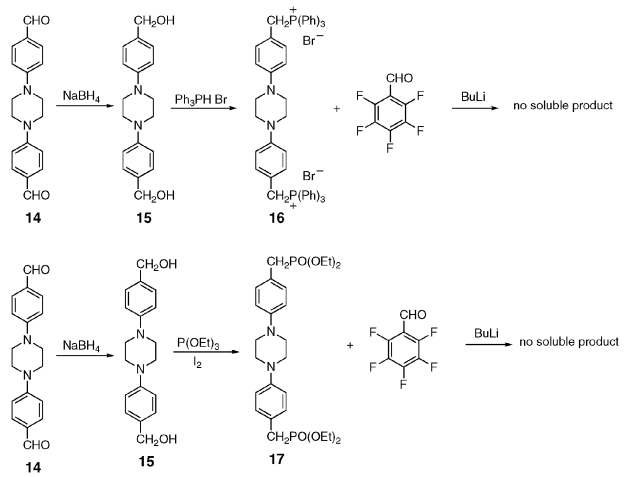


Scheme 4 Reactions of piperazinyl-pentafluoro-stilbenes.

reacted with pentafluoro-benzaldehyde, but it was not possible to isolate the desired product. The outcome of this reaction was an almost insoluble, fluorescent matter. The hypothesis of uncontrolled photo-polymerization of the product, resulting into an insoluble polymer, in principle should be ruled out, because the reaction was carefully carried out in the dark and the work up done in the presence of Erythrosine-B (a quencher for triplet states, involved in the photodimerization) or with Nafion-H®, to protonate the piperazine nitrogen atoms and hindering therefore the [2 + 2] reaction. The low solubility of the products hindered a full characterization; mass spectroscopy, IR spectroscopy and elemental analysis are in agreement with the presence of the desired product, but NMR analysis was not possible, due to the low solubility. We explored also alternative strategies to prepare this bis-stilbene. In a first experiment, the bis-aldehyde **14** was reacted with the phosphorane **5** under standard Wittig conditions, but we obtained the same results observed with the phosphorane. The alcohol **15** was transformed into the bis-phosphonate **17** by reaction with triethyl-phosphite, in the presence of iodine, but compound **17** was found totally unreactive under Wittig–Horner conditions (Scheme 5).

The reactions described so far underline the versatility of pentafluoro-stilbenes towards further functionalization and they widen the potential applications of these compounds. Indeed all the reactions we performed can be exploited as possible strategies for linking these molecules to polymeric matrixes, in particular compound **7** could be used as a photo-reactive unit in side-chain functionalized polymers. On the other side, the preparations of bis-stilbenes showed a puzzling situation: the head-to-tail dimer **13** was easily accessible and we were able to carry out a complete analysis confirming its structure, while it was not possible to isolate and fully characterize the head-to-head dimer, because of the low solubility of the products of the reaction. All the products have been characterized in solution by ^{1}H and ^{19}F NMR, UV-Visible absorption and fluorescence spectroscopy and mass spectroscopy. All the stilbenes are highly fluorescent and present fluorescence maxima between 430 and 450 nm.

All stilbene derivatives described so far (**6a**, **6b**, **7**, **10a**, **10b**, **11**, **12**, and **13**) were exposed to a low power source lamp

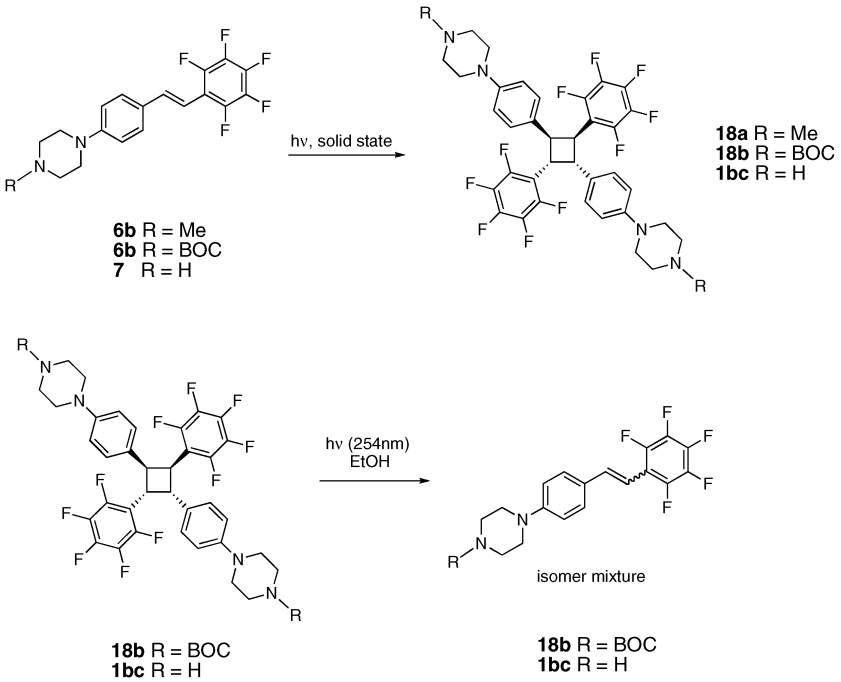


Scheme 5 Attempts to synthesize head-to-head bis-stilbene.

(see Experimental section for details) in order to determine quickly the substrates with solid state reactivity comparable to that of compound **1**. We transformed compounds **6a**, **6b** and **7** into the corresponding cyclobutane derivatives **18a**, **18b** and **18c** in quantitative yield. The ^{1}H NMR analysis showed for all the cyclobutanes a signal system for the hydrogen atoms of cyclobutanic ring centered around 4.5 ppm, and, on the basis of the middle point method proposed, we assigned the cyclobutanes **18a–c** the same configuration as that of **3**. The stilbenes **10a**, **10b**, **11**, **12**, and **13** did not give any cyclization product, even after a very long exposure. These findings clearly suggest that the presence of bulky substituents attached to the stilbene double bond hinders the reactivity of these derivatives, probably because it increases the distance between double bonds involved in the formation of the cyclobutane ring. These results are in line with the observed photochemical inertness found for compound **2**. These data support the idea that there is a limit to the dimension and nature of the substituents present on the stilbene core, which are compatible with the photocyclization, because bulky substituents can destroy the arene–perfluoroarene interactions, responsible for solid-state photocyclization. We fully characterized all new cyclobutane derivatives by ^{1}H and ^{19}F NMR, mass spectroscopy and melting point analysis. All cyclobutanes show UV-Visible absorption bands below 300 nm and are non-fluorescent.

We decided to investigate the retro-cyclization of these cyclobutanes to their parent stilbenes, both by thermal treatment and by UV irradiation (254 nm). We carried out the thermal treatment by heating a toluene solution of **18b** at 160 °C in a closed microwave reactor (power 180 W). After 1 h of irradiation, the cyclobutane **18b** was recovered quantitatively with no traces of stilbene **6b** detected, even by spectrofluorimetry, which underlines the high thermal stability of **18b**. As anticipated, the photocyclization reaction is reversible in solution by irradiation with UV radiation (254 nm). Thus, an ethanol solution of **18b** (3 mg in 10 mL of ethanol) has been irradiated for 1 h and the crude reaction mixture analyzed by ^{1}H-NMR. The analysis showed that the retro-photocyclization occurs with a fairly good yield (**6b**: yield = 63%. **6c**: yield = 57%) but again gave a mixture of both *trans* and *cis* isomers with 10 : 1 ratio respectively (Scheme 6).

The prevalence of the *trans* isomer stimulated us to investigate whether the retro-photocyclization could occur in a polymeric matrix and whether the polymeric matrix can influence the stereoselectivity of the retro-photocyclization, since this possibility is of considerable importance in the development of new optical memories. We preferred to blend the cyclobutane derivative instead of the stilbene into the polymer because in this way the retro-cyclization should produce 'couples' of stilbene molecules able to give again the [2 + 2] photoreaction, while a blend of the stilbene could produce a random distribution of the isolated molecules, hampering the photocyclization. For this investigation we chose poly-methyl-methacrylate (PMMA), because of its high optical quality. We irradiated casted films, prepared from a CH_2Cl_2 solution of PMMA doped with **18b** (5% weight) with UV radiation (254 nm) produced by low-pressure mercury vapor lamp (15 W). We monitored the progress of the reaction



Scheme 6 Photocyclization and cycloreversion of photoreactive stilbenes.

by UV-Visible absorption (Fig. 3) and the results demonstrated that a complete retro-photodimerization is obtained after 1 h of irradiation as shown by the disappearance of the band at 260 nm (of the cyclobutane derivative, curve 1 in Fig. 3) and the appearance of a new band at 340 nm (due to the stilbene absorption, curve 2) as confirmed by comparing this absorption band with that of a cast film of PMMA doped with **6b**, prepared in the same way. In addition, the film becomes fluorescent under 365 nm light and this evidence indicates a successful retro-photodimerization. These results confirm that fluorinated stilbenes can be exploited as active materials for new optical memories. We also tried to determine how many cycles of photodimerization and retro-cyclization could be performed. Thus, on the same sample, we attempted exposure cycles at 365 nm (to transform the stilbene into the cyclobutane) and at 254 nm (to open the cyclobutane). After 20 h of exposure with λ_{exc} = 365 nm (4 W) we observed a reduction of the absorption in the UV-Visible spectrum but not the complete disappearance of absorption band centered at 330 nm (due to the stilbene absorption), therefore suggesting that only a fraction of stilbene was converted into cyclobutane. After that, we carried out irradiation with λ_{exc} = 254 nm, to open the cyclobutane, but after 5 h we did not find any appreciable variation in the absorption spectra (curve 3 in Fig. 3). We attribute the origin of these results to preferential formation of the *cis* isomer during the photolysis reaction, since the TLC analysis of the stilbene extracted from the polymeric matrix showed a higher amount of the *cis* isomer (50% *vs.* 10% observed in alcoholic solution). Also the blue shift of the stilbene absorption maximum in the UV-Visible absorption confirmed the presence of a higher amount of *cis* isomer.

During the retro [2+2] both *cis* and *trans* isomers have equal probability and a 1 : 1 mixture of two isomers is expected. In solution the molecules can move around freely and the *cis* isomer can be converted into the more stable *trans* one and photostationary state is generally enriched with *trans*-isomer. Within the polymeric matrix, the limited mobility of the molecules hinders the *cis–trans* isomerization and therefore this completely explains our findings. This result can have a positive outcome, because the retro-cyclization of cyclobutanes imbedded in polymeric matrixes can be viewed as a mean of obtaining a mixture of olefins enriched in the *cis* isomer, while usually the *trans* isomer is prevalent. Finally, we carried out IR reflectance measurements (see ESI† for a caption of the spectra) on films of PMMA doped with stilbene **6b** and cyclobutane **18b** (8% in weight for both of them). Unfortunately the region of double bond bending (*trans* double bond shows a strong band around 900 cm^{-1}) is partially covered by the stretching and bending modes of the polymeric

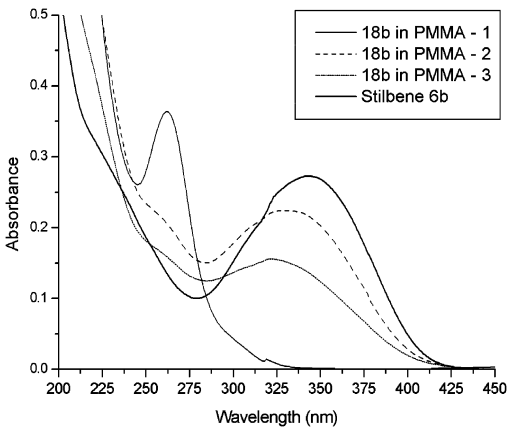


Fig. 3 Absorption spectra of **18b** in PMMA matrix. The different spectra show the conversion of **18b** into the corresponding stilbene, compared with a spectrum of **6b** in PMMA matrix.

matrix and cannot be diagnostic for the analysis of the photodimerization process. However, the PMMA is completely transparent around 1600 cm^{-1}, a region where PMMA doped by stilbene **6b** and that doped with the cyclobutane **18b** show significant differences. In fact, the PMMA doped with stilbene **6b** shows a peak at 1604 cm^{-1}, while the polymer doped with **18b** shows a very weak peak at 1612 cm^{-1}; these signals arise from the stretching vibrations of the C=C bonds of olefins and aromatic rings. The absorption at 1604 cm^{-1} is probably due to stretching of C=C olefinic bond and aromatic double bonds of stilbene, while the peak at 1612 cm^{-1} detected for PMMA doped with cyclobutane is only due to the stretching of aromatic rings. In any case both these signals are clearly distinguishable from those of the polymeric matrix and can be used as possible readout region for an optical memory functions of these compounds. Other parts of the IR spectrum cannot be used to discriminate stilbene-doped PMMA from cyclobutane-doped.

Conclusions

In conclusion, we have synthesized a series of new polyfluoro-amino-stilbenes and analyzed their photochemical behavior in the solid state. A number of these compounds showed a good propensity to give the corresponding cyclobutane photodimers in quantitative yields. Arene–perfluoroarene π–π interactions assure the correct position of the olefinic double bonds, necessary to observe [2 + 2] cyclization. The photocyclization is reversible both in solution and when the cyclobutane is dispersed in a polymeric matrix. A different *cis–trans* stereoselectivity is observed for the stilbenes obtained from retro-cyclization in solution and in polymeric matrix with a preference for the *cis* isomer in the polymeric matrix. Even though the formation of *cis* isomer limits the number of open–closure cycles, the results presented here confirm that fluorinated stilbenes and/or cyclobutanes are potential systems for at least non-rewritable optical data storage devices. The stability of the cyclobutane under heating represents another advantage for such an application. Moreover, the possibility to obtain the *cis* isomer from the ring opening in a polymeric matrix is an interesting result, since usually the photolysis of cyclobutanes in solution affords solely the *trans* isomer. Thus the incorporation of cyclobutanes in polymeric matrices can be a useful method to drive the retro-cyclization in producing the *cis* isomers, since this result is hard to obtain in solution, where, for steric and stability reasons, the *trans* isomer is always the preferred one.

Experimental section

Methods and materials

Melting points were determined with a melting point apparatus in open tubes and are uncorrected. ^{1}H NMR and ^{19}F NMR spectra were collected at rt, in $CDCl_3$. Chemical shifts are given as parts per million from tetramethylsilane and *J* values are given in Hertz. ^{19}F NMR spectra were collected using $CFCl_3$ as internal standard. Photochemical reactions were carried out with a 5 W lamp, equipped with two bulbs (254 nm and 365 nm); solid and solution (within quartz cuvettes) samples were held at 10 cm from the bulbs. Compounds **1**, **2**, **4a**, **b**, **5**, **14** were prepared as described in the literature. nBuLi (1.6 M hexane solution) was purchased from Merck Co. and titrated just before use. Tetrahydrofuran (THF) was dried by refluxing in the presence of Na/benzophenone. All manipulations were performed under an inert gas (nitrogen). Flash chromatography was performed with silica gel 230–400 mesh.

Single crystal X-ray data were measured at room temperature (298 K) on a Bruker SMART CCD diffractometer using Mo-K_α radiation, λ = 0.71073 Å. The structure was solved by direct methods and refined by full-matrix least-squares against Fo2 using SHELXL97 software.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model.†

AFM imaging was performed with a Nanoscope IIIa AFM (VEECO) in contact mode with oxide sharpened Si_3N_4 tips of nominal 0.06 N m^{-1} force constant. Force applied to the crystal surface by the tip was minimized to reduce influence of scanning on steps. Scan rates were in the range 3–4 Hz. All images are unfiltered. The photoreaction was triggered by an optical fiber halogen lamp filtered with a white screen to reduce the amount of photons reaching the sample surface in order to be able to follow the surface reaction with the AFM.

Syntheses

Synthesis of compounds 6a and 6b. 0.5 mmol of the aldehyde (**4a** or **4b**) were added at 0 °C, under an inert gas, to a yellow THF solution (10 mL) of the phosphorane **5** (0.5 mmol prepared as described in the literature). The mixture was allowed to react at room temperature and the progress of the reaction was monitored by TLC (eluent: diethyl ether/light petroleum ether, 3 : 7). The reaction was carried out in the dark. The reaction was complete after 15 h and then was quenched by addition of few drops of water. The solvent was distilled under reduced pressure, affording a bright yellow solid. The solid was taken up with CH_2Cl_2 (20 mL), and the organic layer was washed twice with distilled water. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by dry flash chromatography (eluent: light petroleum ether/ethyl acetate 3 : 7) affording the desired product.

Compound **6a**. Yellow greenish solid. Reaction yield: 60%. Mp 175 °C. IR (nujol): ν (cm^{-1}) = 1603 (ν, HC=CH *trans*), 1350.5 (ν, C_{arom}-N), 957 (out of plane deformation C-H *trans*). UV-Vis (CH_2Cl_2): λ_{max} = 355 nm. Fluorescence (CH_2Cl_2): λ_{max} = 455 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H, CH_3), 2.57 (t, 4H, CH_2 of piperazine), 3.28 (t, 4H, CH_2 of piperazine), 6.80 (d, 1H, C_6F_5-CH=C*H*-Ar), 6.91 (d, 2H, aromatic ring), 7.29 (d, 1H, C_6F_5-C*H*=CH-Ar), 7.43 (d, 2H, aromatic ring). ^{19}F NMR (75 MHz, $CDCl_3$): δ = −143.86 (m, 2F, F_{ortho}), −158.56 (m, 1F, F_{para}), −163.89 (m, 2F, F_{meta}). MS(EI): *m*/*z* = 368 $[C_{19}H_{17}F_5N_2]^+$. Elemental analysis for $C_{19}H_{17}F_5N_2$: calcd C 61.95, H 4.65, N 7.61%; found C 61.89, H 4.35, N 7.57%.

Compound **6b**. Yellow greenish solid. Reaction yield: 71%. Mp 171 °C. IR (nujol): ν (cm^{-1}) = 1696.5 (ν, C=O), 1605 (ν, HC=CH *trans*), 1370 (ν, C_{arom}-N), 957 (out of plane deformation C-H *trans*). UV-Vis (CH_2Cl_2): λ_{max} = 328 nm. Fluorescence (CH_2Cl_2): λ_{max} = 446 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51 (s, 9H, C-CH_3), 3.25 (t, 4H, CH_2 of piperazine), 3.64 (t, 4H, CH_2 of piperazine), 6.85 (d, 1H, C_6F_5-CH=C*H*-Ar), 6.97 (d, 2H, aromatic ring), 7.32 (d, 1H, C_6F_5-C*H*=CH-Ar), 7.48 (d, 2H, aromatic ring). ^{19}F NMR (75 MHz, $CDCl_3$): δ = −143.73 (d, 2F, F_{ortho}), −158.14 (t, 1F, F_{para}), −163.69 (t, 2F, F_{meta}). MS(EI): m/z = 454 $[C_{23}H_{23}F_5N_2O_2]^+$. Elemental analysis for $C_{23}H_{23}F_5N_2O_2$: calcd C 60.79, H 5.10, N 6.16%; found C 60.75, H 5.01, N 6.12%.

Alternative synthesis for compound 6a. (a) *Synthesis of p-(4-methyl-piperazinyl)-benzyl-alcohol* (compound **8**): 1.554 g of *p*-(4-methyl-piperazinyl)-benzaldehyde (**4a**) were dissolved in 25 mL of EtOH and 336 mg of $NaBH_4$ were added, keeping the temperature in the range 18–20 °C, then the solution was heated at 40 °C for 1 h. The solution was then neutralized and extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure, affording the desired alcohol (pale yellow solid). Yield: 73%. Mp 102–103 °C. IR (nujol): ν (cm^{-1}) = 3186 broad (ν, OH). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (broad, 1H, O*H*), 2.35 (s, 3H, CH_3), 2.57 (t, 4H, J = 5.1, CH_2 of piperazine), 3.18 (t, 4H, J = 5.1 Hz, CH_2 of piperazine), 6.91 (d, 4H, J = 8.5, aromatic ring), 7.27 (d, 4H, J = 8.5, aromatic ring). MS(EI): m/z = 206 $[C_{12}H_{18}N_2O]^+$. Elemental analysis for $C_{12}H_{18}N_2O$: calcd C 69.87, H 8.80, N 13.58%; found C 69.01, H 8.50, N 13.0%. (b) *Synthesis of p-(4-methyl-piperazinyl)-benzyl-triphenyl-phosphonium bromide* (compound **9**): 711 mg of *p*-(4-methyl-piperazinyl)-benzyl alcohol (**8**) and 3.847 g of triphenyl-phosphonium bromide were suspended in anhydrous CH_2Cl_2. The mixture was refluxed for 5 h, then the solvent was removed under reduced pressure. The yellow solid was dissolved in water and then extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure, affording the desired product (white solid). Yield: 67%. IR (nujol): ν (cm^{-1}) = 1342 broad (ν, C_{arom}-N), 1516 (ν, CH_2-P), 1436 (ν, P-C_6H_5), 1608 (ν, C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 2.57 (m, 4H, CH_2 of piperazine), 3.15 (m, 4H, CH_2 of piperazine), 5.25 (d, 2H, J = 13.5, CH_2-PPh_3), 6.69 (d, 2H, J = 8.5, aromatic ring), 6.97 (d, 2H, J = 8.5, aromatic ring), 7.64–7.78 (m, 15 H, -P(C_6H_5)$_3$). ^{31}P NMR (300 MHz, $CDCl_3$): δ = 23.71 (s, -*P*Ph_3). Elemental analysis for $C_{30}H_{32}BrN_2P$: calcd C 67.80, H 6.07, N 5.27%; found C 67.50, H 6.10, N 5.10%. (c) *Synthesis of 2,3,4,5,6-pentafluoro-4′-(4-methyl-piperazinyl)-stilbene* (compound **6a**): 287 mg of *p*-(4-methyl-piperazinyl)-benzyl-triphenyl-phosphonium bromide (**9**) were suspended in 4 mL of anhydrous THF; 0.58 mL of n-BuLi (1.194 M) were added dropwise, keeping the temperature at 0 °C, obtaining a dark red solution. The solution was stirred for 30 min at rt, then 114 mg of pentafluoro-benzaldehyde were added. The mixture was allowed to react for 3 h in the dark, the reaction was quenched with few drops of water and the solvent evaporated under reduced pressure. The yellow crude solid was then taken up with CH_2Cl_2 and washed with water. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by column chromatography (eluent: CH_2Cl_2/MeOH 9 : 1), affording the desired product (yield: 38%).

Compound **7**. A solution of 0.5 mL of CF_3COOH in anhydrous CH_2Cl_2 (0.5 mL) was added to a solution of **6b** (0.3 mmol) in anhydrous CH_2Cl_2 (0.5 mL). The solution was stirred for 5 h at room temperature in the dark, then was quenched with an aqueous saturated solution of $NaHCO_3$. The aqueous layer was then extracted with CH_2Cl_2, the organic phase dried with Na_2SO_4, and the solvent evaporated under reduced pressure. The crude solid was purified by column chromatography (eluent: light petroleum ether/ethyl acetate 3 : 7) affording the desired product. Pale yellow solid. Reaction yield 65%. Mp 168–169 °C. IR (nujol): ν (cm^{-1}) = 3436 (ν, N-H), 1603 (ν, HC=CH *trans*), 1377 (ν, C_{arom}-N), 960 (out of plane deformation C-H *trans*). UV-Vis (CH_2Cl_2): λ_{max} = 319 nm. Fluorescence (CH_2Cl_2): λ_{max} = 445 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.81 (t, 4H, CH_2 of piperazine), 3.13 (t, 4H, CH_2 of piperazine), 6.82 (d, 1H, C_6F_5-CH=C*H*-Ar), 6.94 (d, 2H, aromatic ring), 7.31 (d, 1H, C_6F_5-C*H*=CH-Ar), 7.51 (d, 2H, aromatic ring). ^{19}F NMR (75 MHz, $CDCl_3$): δ = −143.62 (d, 2F, F_{ortho}), −157.04 (t, 1F, F_{para}), −163.87 (m, 2F, F_{meta}). Elemental analysis for $C_{18}H_{15}F_5N_2$: calcd C 61.02, H 4.27, N 7.91%; found C 60.75, H 4.15, N 7.85%.

Synthesis of compounds 10a and 10b. To a solution of stilbene **6b** (0.1 mmol) and the proper piperidine (0.15 mmol) in anhydrous DMSO (13 mL) was added Na_2CO_3 (0.15 mmol). The solution was heated at 90 °C for 33 h in the dark, then was added water and the resulting solution was extracted with ethyl acetate. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by dry flash chromatography (eluent: light petroleum ether/ethyl acetate 1 : 1 and then methanol/ethyl acetate 1 : 1) affording the desired product.

Compound **10a**. Yellow solid. Reaction yield: 63%. Mp 165–166 °C. UV-Vis (CH_2Cl_2): λ_{max} = 346 nm. Fluorescence (CH_2Cl_2): λ_{max} = 438 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 9H, C-CH_3), 2.31 (broad, 1H, N-H), 3.08 (s, 4H, CH_2 of methyl-piperazine), 3.24 (t, 4H, CH_2 of BOC-piperazine), 3.32 (s, 4H, CH_2 of methyl-piperazine), 3.63 (t, 4H, CH_2 of BOC-piperazine), 6.90 (d, 1H, C_6F_5-CH=C*H*-Ar), 6.94 (d, 2H, aromatic ring), 7.36 (d, 1H, C_6F_5-C*H*=CH-Ar), 7.48 (d, 2H, aromatic ring). Elemental analysis for $C_{27}H_{32}F_4N_4O_2$: calcd C 62.30, H 6.20, N 10.76%; found C 62.25, H 6.22, N 10.68%.

Compound **10b**. Yellow solid. Reaction yield: 29%. Mp 172–174 °C. UV-Vis (CH_2Cl_2): λ_{max} = 347 nm. Fluorescence (CH_2Cl_2): λ_{max} = 436 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 9H, C-CH_3), 2.50 (s, 3H, N-CH_3), 2.74 (s, 4H, CH_2 of methyl-piperazine), 3.24 (t, 4H, CH_2 of BOC-piperazine), 3.44 (s, 4H, CH_2 of methyl-piperazine), 3.63 (t, 4H, CH_2 of BOC-piperazine), 6.86 (d, 1H, C_6F_5-CH=C*H*-Ar), 6.94 (d, 2H, aromatic ring), 7.36 (d, 1H, C_6F_5-C*H*=CH-Ar), 7.48

(d, 2H, aromatic ring). Elemental analysis for $C_{28}H_{34}F_4N_4O_2$: calcd C 62.91, H 6.41, N 10.48%; found C 62.56, H 6.35, N 10.44%.

Compound **11**. To a solution of stilbene **7** (0.17 mmol) and the *p*-fluoro-benzaldehyde (0.53 mmol) in anhydrous DMSO (3 mL) was added K_2CO_3 (0.2 mmol). The solution was heated at 90 °C for 20 h in the dark, then was added water (10 mL) and the resulting solution was extracted with ethyl acetate. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by dry flash chromatography (eluent: light petroleum ether/ethyl acetate 2 : 8) affording the desired product. Yellow solid. Reaction yield 23% Mp: decomposition starting at 200 °C. IR (nujol): ν (cm^{-1}) = 1685 (ν, C=O), 1600 (ν, HC=CH *trans*), 1377 (ν, C_{arom}-N), 956 (out of plane deformation C-H *trans*). UV-Vis (CH_2Cl_2): λ_{max} = 339 nm. Fluorescence (CH_2Cl_2): λ_{max} = 444 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.47 (t, 4H, CH_2 of piperazine), 3.63 (t, 4H, CH_2 of piperazine), 6.86 (d, 1H, C_6F_5-CH=C*H*-Ar), 6.99 (d, 2H, aromatic ring of stilbene), 7.00 (d, 2H, aromatic ring of benzaldehyde), 7.40 (d, 1H, C_6F_5-C*H*=CH-Ar), 7.51 (d, 2H, aromatic ring of stilbene), 7.82 (d, 2H, aromatic ring of benzaldehyde), 9.84 (s, 1H, CHO). MS(EI): m/z = 458 $[C_{25}H_{19}F_5N_2O]^+$. Elemental analysis for $C_{25}H_{19}F_5N_2O$: calcd C 65.50, H 4.18, N 6.11%; found: C 65.32, H 4.11, N 6.05%.

Compound **12**. To a solution of stilbene **10a** (0.088 mmol) and the *p*-fluoro-benzaldehyde (0.123 mmol) in anhydrous DMSO (15 mL) was added NaH (0.111 mmol). The solution was heated at 90 °C for 20 h in the dark, then was added water (25 mL) and the resulting solution was extracted with ethyl acetate. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by dry flash chromatography (eluent: dichloromethane/ethyl acetate 96 : 4) affording the desired product. Yellow solid. Reaction yield: 48%. Mp 183–184 °C. UV-Vis (CH_2Cl_2): λ_{max} = 336 nm. Fluorescence (CH_2Cl_2): λ_{max} = 427 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 9H, C-CH_3), 3.26 (t, 4H, CH_2 of BOC-piperazine), 3.48 (t, 4H, CH_2 of piperazine), 3.57 (t, 4H, CH_2 of BOC-piperazine), 3.66 (t, 4H, CH_2 of piperazine), 6.92 (d, 1H, C_6F_5-CH=C*H*-Ar), 7.01 (d, 2H, aromatic ring of stilbene), 7.10 (d, 2H, aromatic ring), 7.38 (d, 1H, C_6F_5-C*H*=CH-Ar), 7.49 (d, 2H, aromatic ring of stilbene), 7.82 (d, 2H, aromatic ring), 9.85 (s, 1H, CHO). Elemental analysis for $C_{34}H_{36}F_4N_4O_3$: calcd C 65.37, H 5.81, N 8.97%; found C 65.25, H 5.75, N 8.85%.

Compound **13**. 0.04 mmol of the formyl-phenyl-stilbene **12** were added at 0 °C, under an inert gas, to a THF solution (12 mL) of the phosphorane **5** (0.05 mmol prepared as described in the literature). The mixture was allowed to react at room temperature and the progress of the reaction was monitored by TLC (eluent: diethyl ether/light petroleum ether, 3 : 7). The reaction was carried out in the dark. The reaction was complete after 13 h and then was quenched by addition of 15 mL of water. The solvent was distilled under reduced pressure, affording a bright yellow solid. The solid was taken up with CH_2Cl_2 (10 mL), and the organic layer was washed twice with distilled water. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography (eluent: CH_2Cl_2/ethyl acetate 95 : 5) affording the desired product. Yellow solid. Reaction yield: 50%. UV-Vis (CH_2Cl_2): λ_{max} = 338 nm. Fluorescence (CH_2Cl_2): λ_{max} = 458 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 9H, C-C*H*$_3$), 3.18 (t, 4H, J = 1.6 Hz, CH_2 of N-BOC piperazine), 3.39 (m, 4H, CH_2 of piperazine), 3.42 (t, 4H, J = 1.6 Hz, CH_2 of N-BOC piperazine), 6.54 (m, 4H, CH_2 of piperazine), 6.76–7.12 (m, 6H, olefinic and aromatic), 7.31–7.36 (m, 2H, olefinic), 7.44 (d, 2H, J = 2.9 Hz, aromatic), 7.47 (d, 2H, J = 3.0, aromatic). ^{19}F NMR (75 MHz, tetrachloroethane-D_2): δ = −139.0 (m, 2F, tetrafluoro-phenyl ring), −143.73 (m, 2F, F_{ortho}), −150.17 (m, 2F, tetrafluoro-phenyl ring), −156.51 (m, 1F, F_{para}), −161.04 (t, 2F, F_{meta}). Elemental analysis for $C_{41}H_{37}F_9N_4O_2$: calcd C 62.43, H 4.73, N 7.10%; found C 62.35, H 4.65, N 7.01%.

Compound **15**. 7.326 mmol of bis-aldehyde **14** were suspended in 120 mL of EtOH and 14.3 mmol of $NaBH_4$ were added, keeping the temperature in the range 18–20 °C, then the stirred at rt for 3 h. The solution was then neutralized with diluted HCl and extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure, affording the desired alcohol. Pale yellow solid. Yield: 95%. Mp 197–198 °C. IR (nujol): ν (cm^{-1}) = 3256 broad (ν, OH). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.37 (2, 8H, CH_2 of piperazine), 4.41–4.94 (s, 4H, CH_2-OH), 7.00 (d, 4H, J = 1.2, aromatic), 7.32 (d, 4H, J = 1.2, aromatic). Elemental analysis for $C_{18}H_{22}N_2O_2$: calcd C 72.46, H 7.43, N 9.39%; found C 72.28, H 7.35, N 9.35%.

Compound **16**. 0.735 mmol of **15** with 3.011 mmol of triphenyl-phosphonium bromide $HPPh_3Br$ were suspended in anhydrous toluene. The mixture was heated at 75 °C for 7 h, then the solvent was removed under reduced pressure. The pink solid was taken up with CH_2Cl_2 and then washed with an aqueous saturated solution of $NaHCO_3$. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure, affording the desired product. White solid. Yield: 68%. Mp 297–298 °C. IR (nujol): ν (cm^{-1}) = 1352 broad (ν, C_{arom}-N), 1516 (ν, CH_2-P), 1436 (ν, P-C_6H_5), 1604 (ν, C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.21 (s, H, CH_2 of piperazine), 5.34 (d, 4H, J = 15.1, CH_2-P), 6.45 (d, 4H, J = 8.6, aromatic), 7.00 (d, 4H, J = 8.6, aromatic), 7.61–7.80 (m, 30H, -P(C_6H_5)$_3$). ^{31}P NMR (300 MHz, $CDCl_3$): δ = 23.94 (s, -*P*Ph_3). Elemental analysis for $C_{53}H_{48}Br_2N_2P_2$: calcd C 68.10, H 5.18, N 3.00%; found C 68.02, H 5.49, N 2.85%.

Compound **17**. 0.69 mmol of **15** were suspended in 6.4 mL of triethyl-phosphite at 0 °C and 1.4 mmol of iodine were added portionwise. The reaction was stirred at rt for 15 h, then the triethyl-phosphite was evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: ethyl acetate/methanol 9 : 1, affording the desired product. Pale yellow solid. Reaction yield 20%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, 12H, CH_3), 3.10 (d, 4H, -P-CH_2-Ar), 3.35 (s, 8H, CH_2 of piperazine), 4.04 (m, 8H, -CH_2-CH_3), 6.96 (d, 4H, aromatic), 7.24 (d, 4H, aromatic). MS(EI): m/z = 538 $[C_{26}H_{40}N_2O_6P_2]^+$,

498, 401. Elemental analysis for $C_{26}H_{40}N_2O_6P_2$: calcd C 57.98, H 7.49, N 5.20%; found C 57.66, H 7.32, N 5.05%.

Synthesis of compounds 3, 18a, 18b, and 18c. 40 mg of the stilbene are put on a microscope slab and exposed to a 20 W tungsten light bulb for 15 h. This solid state reaction is monitored by TLC.

Compound **3**. White solid. Quantitative yield. Mp 145–146 °C. IR (nujol): ν (cm^{-1}) = 1232 (ν, C-N), 1011.5 (ν, C-F). UV-Vis (CH_2Cl_2): λ_{max} = 400 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90 (12H, s, CH_3N), 4.73 (4H, s, CH of cyclobutane), 6.64 (d, 4H, J = 8.8, aromatic ring), 7.07 (d, 4H, J = 8.8, aromatic ring). ^{19}F NMR (75 MHz, $CDCl_3$): δ = −141.91 (m, 4F, F_{ortho}), −157.26 (m, 2F, F_{para}), −163.43 (m, 4F, F_{meta}). Elemental analysis for $C_{32}H_{24}F_{10}N_2$: calcd C 61.34, H 3.86, N 4.47%; found C 61.15, H 3.90, N 4.59%.

Compound **18a**. White solid. Quantitative yield. Mp 173–174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (6H, s, CH_3N), 2.63 (m, 8H, CH_2 of piperazine), 3.21 (t, 8H, J = 4.9, CH_2 of piperazine), 4.79 (s, 4H, CH of cyclobutane), 6.81 (d, 4H, J = 8.7, aromatic ring), 7.11 (d, 4H, J = 8.7, aromatic ring). ^{19}F NMR (75 MHz, $CDCl_3$): δ = −141.88 (m, 2F, F_{para}), −156.71 (m, 4F, F_{meta}), −163.16 (m, 4F, F_{ortho}). Elemental analysis for $C_{38}H_{34}F_{10}N_4$: calcd C 61.95, H 4.65, N 7.61%; found C 61.74, H 4.48, N 7.54%.

Compound **18b**. White solid. Quantitative yield. Mp 170–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 18H, C-CH_3), 3.11 (t, 8H, J = 5.0, CH_2 of piperazine), 3.59 (m, 8H, CH_2 of piperazine), 4.81 (s, 4H, CH of cyclobutane), 6.89 (d, 4H, J = 8.5, aromatic ring), 7.14 (d, 4H, J = 8.5, aromatic ring). ^{19}F NMR (75 MHz, $CDCl_3$): δ = −142.58 (m, 2F, F_{para}), −157.78 (m, 4F, F_{meta}), −163.47 (m, 4F, F_{ortho}). Elemental analysis for $C_{46}H_{46}F_{10}N_4O_4$: calcd C 60.79, H 5.10, N 6.16%; found C 60.65, H 5.21, N 6.12%.

Compound **18c**. White solid. Quantitative yield. Mp 171–172 °C. IR (nujol): ν (cm^{-1}) = 3434 (ν, N-H), 1377 (ν, C_{arom}-N). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (broad, 8H, CH_2 of piperazine), 3.07 (broad, 8H, CH_2 of piperazine), 4.77 (broad, 4H, CH of cyclobutane), 6.82 (d, 4H, J = 8.6, aromatic ring), 7.15 (d, 4H, J = 8.6, aromatic ring). ^{19}F NMR (75 MHz, $CDCl_3$): δ = −141.39 (t, 2F, F_{para}), −156.14 (m, 4F, F_{meta}), −163.29 (d, 4F, F_{ortho}). Elemental analysis for $C_{36}H_{30}F_{10}N_4$: calcd C 61.02, H 4.27, N 7.91%; found C 60.85, H 4.15, N 7.85%.

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