

Benzo-2,1,3-thiadiazole-based, highly dichroic fluorescent dyes for fluorescent host–guest liquid crystal displays†

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The highly dichroic fluorescent dyes 4,7-bis(*p*-alkoxyphenyl)-, 4,7-bis(*p*-alkoxymethylphenyl)-, and 4,7-bis(*p*-alkoxycarbonylphenyl)-2,1,3-benzothiadiazoles have been synthesized and their dichroic properties evaluated. A solution of the former dye dispersed in the commercial liquid crystalline MLC-2039 host phase showed a dichroic ratio value for fluorescence up to 9.1.

Introduction

Passive full-color liquid crystal displays (LCDs) consume appreciable electric power of back light systems. Since this is usually supplied by batteries of limited capacity, the development of less energy-consuming displays is required before they can be used in mobile communication tools. Within this context, fluorescent dye (guest)/LC (host) systems in such displays seem attractive.¹ For their realization it is crucial to develop strongly fluorescent dyes with highly dichroic properties, as has also already been the case for passive-type full-color LCDs, where dichroic absorption dyes are being used.^{2–4}

The dichroism of dyes is a characteristic of the anisotropy of the molecular transition moment in either absorption or emission. When a dichroic dye with a geometric anisotropy is dissolved in a nematic liquid crystal, the dye molecule tends to arrange itself in such a way that its long molecular axis aligns along the LC director and a change of color intensity is obtained by controlling the direction of the LC molecules (Fig. 1). A rod-like, long molecular structure is favorable for a strongly dichroic dye. In principle, the design of dichroic fluorescent molecules follows the same guidelines needed for the creation of highly dichroic absorption dyes.^{4a,b} In addition, it is necessary for the molecules to be strongly fluorescent, and the fluorescence should not be quenched by other molecules or by the LC matrix itself. In general, absorption dyes with a dichroic ratio (*N*) of more than 8.0 are required for practical use of the absorption dyes in LCDs. Some fluorescent compounds have been shown to be dichroic⁵ in LC media, albeit partly with insufficient dichroic ratios.

This paper describes the design, synthesis and evaluation of new heterocyclic fluorescent dyes with sufficiently large dichroic ratios to make them feasible for use in commercial displays. The 4,7-diphenyl-substituted benzo-2,1,3-thiadiazole substructure was chosen as the core unit, since 4,7-diphenylbenzo-2,1,3-thiadiazole (**1**) itself is strongly fluorescent in solution ($\Phi_{\text{FL}} = 0.74$) as well as in the solid state. We expected that the introduction of long alkyl chains in the *para* positions of the

phenyl groups would extend the length of the molecule and hence increase its solubility in LC media and its dichroic ratio (Fig. 2).

Results and discussion

Synthesis

Compounds **4**, **8** and **12** were synthesized as shown in Scheme 1. 4,7-Bis(*p*-alkoxyphenyl)benzo-2,1,3-thiadiazoles (**4a–g**) were prepared by the Suzuki-type coupling reaction⁶ of the corresponding *p*-alkoxyphenylboronic acids (**3**) with 4,7-dibromo-2,1,3-benzothiadiazole (**2**).⁷ The coupling reaction of **2** with *p*-formylphenylboronic acid (**5**)⁸ gave the bis(*p*-formylphenyl) derivative **6**, which was converted to the desired bis(*p*-alkoxymethylphenyl)benzo-2,1,3-thiadiazoles (**8a–e**) via reduction and subsequent alkylation. The bis(*p*-carboxyphenyl) derivative **10**

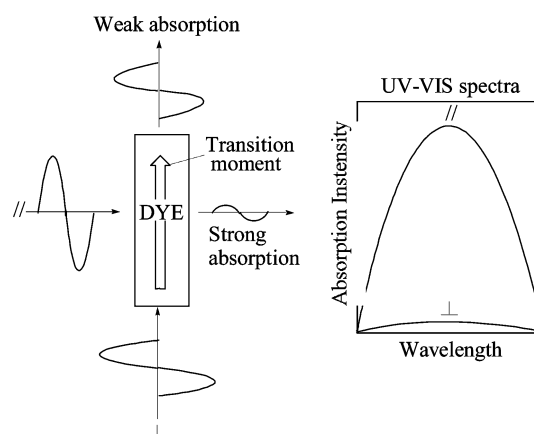


Fig. 1 UV-VIS spectra of an idealized negative dichroic absorption dye.

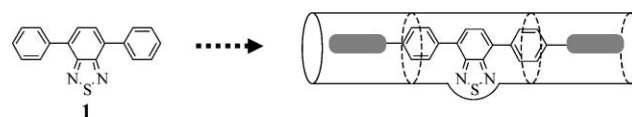
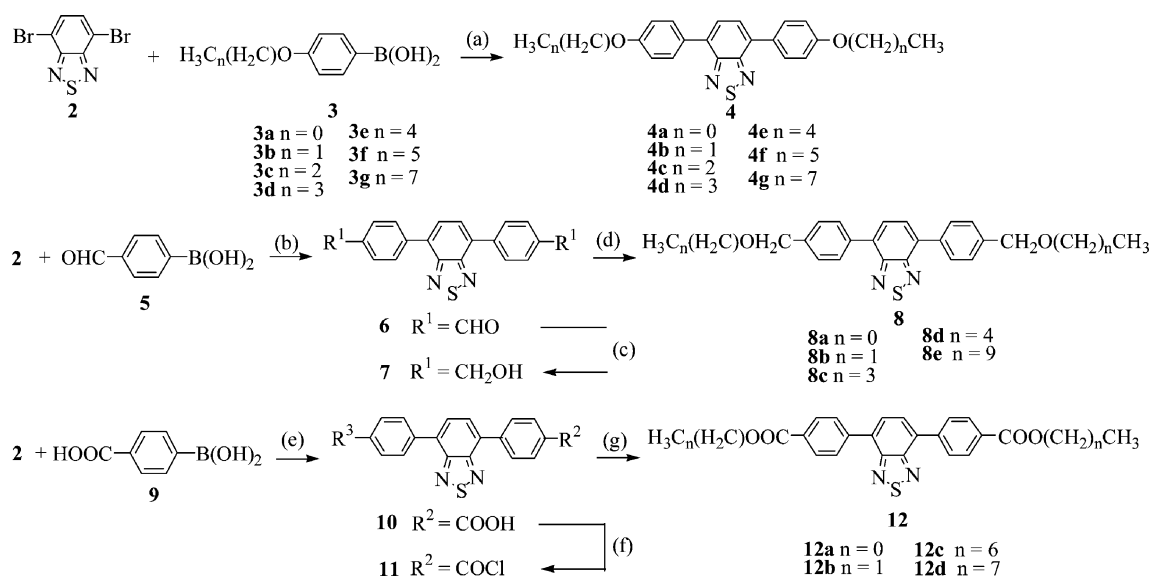


Fig. 2 Schematic representation of an improved fluorescent dye based on 4,7-diphenyl-2,1,3-benzothiadiazole (**1**).

† Electronic supplementary information (ESI) available: general experimental details and synthesis methods for compounds **4**, **6**, **7**, **8**, **10**, **11** and **12**. See <http://www.rsc.org/suppdata/jm/b4/b402645d/>



Scheme 1 Reagents and conditions: (a) benzene/EtOH, Pd(PPh₃)₄, 2 M Na₂CO₃; (b) toluene/EtOH, Pd(PPh₃)₄, 2 M Na₂CO₃; (c) MeOH, NaBH₄; (d) DMSO, R³X, KOH; (e) CH₃CN/EtOH, Pd(PPh₃)₄, 2 M Na₂CO₃; (f) ClCH₂CH₂Cl, SOCl₂; (g) R⁴OH, KOH.

was prepared by the coupling reaction of **2** with *p*-carboxyphenylboronic acid (**9**).⁹ Esterification of **10** to **12a–d** was achieved *via* the corresponding acyl chloride **11**.

UV-Vis and fluorescence spectra of compounds **4**, **8** and **12**

The absorption and fluorescence spectral data of **4**, **8** and **12** are summarized in Table 1. In **4a–g**, the *p*-alkoxy groups cause a large red shift of the absorption and fluorescence maxima ($\Delta\lambda_{\text{max}} = 30\text{--}32$ nm and $\Delta F_{\lambda_{\text{max}}} = 52\text{--}57$ nm), as compared to 4,7-diphenylbenzo-2,1,3-thiadiazole (**1**) ($\lambda_{\text{max}} = 379$ nm, $F_{\lambda_{\text{max}}} = 490$ nm). Smaller red shifts were observed for *p*-alkoxymethyl-substituted **8a–e**. In contrast, substitution of **1** with electron-withdrawing ester groups, as in **12a–d**, causes a blue shift. Similar substituent effects have been characteristically observed in the corresponding 4,7-diaryl-1,2,5-thiadiazolo- and oxadiazolo-pyridines.¹⁰ Such effects of substituents

can be used to obtain different colors in the light emission. Compounds **4** (yellow), **8** (green) and **12** (blue) are all strongly fluorescent, both in solution ($\Phi_{\text{FL}} = 0.69\text{--}0.89$) and in the solid state. For all compounds **4**, **8** and **12**, the wavelength of absorption and the fluorescence maxima are independent of the length of the alkyl chains. This is an advantage when creating a fluorescent LC cell by mixing the dyes with different chain lengths, as the purity of the color is not impaired.

Polarized absorption and emission spectra of **4**, **8**, and **12** in nematic LC media. Determination of the dichroic ratio of the compounds

The polarized absorption and emission spectra of **4**, **8** and **12** in commercial LC media (see below) were measured in cells constructed of two glass plates, the surfaces of which were coated with a thin polyimide layer, which was rubbed in one direction to give a homogeneous planar orientation of the dye and liquid crystal host phase. For the LC media, nematic liquid crystals were chosen with positive or negative dielectric anisotropies. The dyes **4**, **8** and **12** were dissolved in the liquid crystalline medium at a concentration of 0.5% w/w. The cell thickness was controlled by using silicon balls of 50 μm diameter. Measurement of the absorption and fluorescence polarization spectra was carried out by irradiation with a tungsten halogen lamp and a black-light blue fluorescent lamp, parallel and perpendicular to the rubbing. The spectra were reproducible in successive measurements. This indicates that the dye does not crystallize or demix from the LC host upon irradiation, indicating that the nematic mesophase of the host LC is not destabilized by the guest dye.

The dichroic ratios (N) of the guest dyes **4**, **8** and **12** in the LC hosts were determined from the spectra, using eqns. (1) and (2):

$$N_A = A_{\parallel}/A_{\perp} \quad (1)$$

$$N_F = F_{\parallel}/F_{\perp} \quad (2)$$

where N_A is the dichroic ratio of absorption, A_{\parallel} the absorbance for in parallel irradiation, A_{\perp} the absorbance for perpendicular irradiation, N_F the dichroic ratio of fluorescence, F_{\parallel} the fluorescence intensity for parallel irradiation, and F_{\perp} the fluorescence intensity for perpendicular irradiation.

Four different commercial liquid crystals were used: cyano-substituted ZLI-1565, fluoro-substituted ZLI-4792 and cyano-substituted E-8 are LCs with positive dielectric anisotropic

Table 1 Absorption and fluorescence data of 4,7-di(4-substituted phenyl)-2,1,3-benzothiadiazoles **4**, **8**, **12**^{a,b,c}

| Compound | $\lambda_{\text{max}}/\text{nm}$ | $\log \epsilon$ | $F_{\lambda_{\text{max}}}/\text{nm}$ | Φ_{FL} |
|------------|----------------------------------|-----------------|--------------------------------------|--------------------|
| 4a | 409 | 4.08 | 542 | 0.78 |
| 4b | 410 | 4.07 | 546 | 0.75 |
| 4c | 410 | 4.07 | 546 | 0.72 |
| 4d | 410 | 4.07 | 546 | 0.75 |
| 4e | 411 | 4.07 | 547 | 0.75 |
| 4f | 411 | 4.08 | 547 | 0.69 |
| 4g | 412 | 4.08 | 547 | 0.69 |
| 8a | 384 | 4.05 | 505 | 0.75 |
| 8b | 385 | 4.07 | 506 | 0.73 |
| 8c | 385 | 4.06 | 505 | 0.75 |
| 8d | 387 | 4.06 | 506 | 0.75 |
| 8e | 387 | 4.06 | 506 | 0.76 |
| 12a | 376 | 4.21 | 464 | 0.87 |
| 12b | 377 | 4.21 | 465 | 0.89 |
| 12c | 377 | 4.21 | 466 | 0.87 |
| 12d | 377 | 4.21 | 466 | 0.86 |

^a $c = 1.00 \times 10^{-4}$ M in CH₂Cl₂ (absorption); $c = 1.00 \times 10^{-6}$ M in CH₂Cl₂ (fluorescence). ^b Fluorescence spectra were obtained from the excitation of the molecules at the λ_{max} observed in the UV-VIS spectra. ^c Fluorescence quantum yield (Φ_{FL}) of **4** was determined using rhodamine B in EtOH ($c = 1.00 \times 10^{-6}$ M) as the standard ($\Phi_{\text{FL}} = 0.65$). The quantum yields of **8** and **12** were determined with quinine bisulfate dihydrate in 1 N sulfuric acid ($c = 1.00 \times 10^{-6}$ M) as the standard ($\Phi_{\text{FL}} = 0.55$).

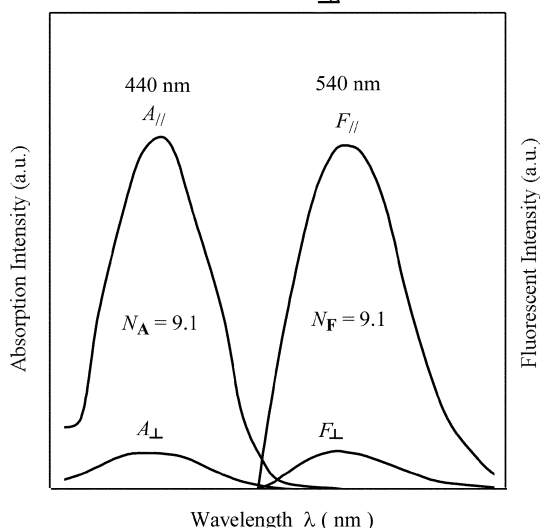
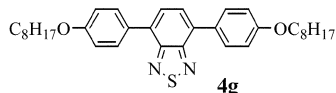


Fig. 3 Polarized absorption and fluorescence spectra of **4g**. Compound **4g** was dissolved in a commercial liquid crystal MLC-2039 at a concentration of 0.5% w/w. Measurement of the polarization spectra was carried out by irradiation with a tungsten halogen lamp and a black-light blue fluorescent lamp, parallel and perpendicular to the rubbing. The dichroic ratios were determined from the formula: $N_A = A_{||}/A_{\perp}$ ($\lambda = 440$ nm), $N_F = F_{||}/F_{\perp}$ ($\lambda = 540$ nm). $A_{||}$ and A_{\perp} are the absorption intensities in the direction parallel and perpendicular to the dye molecule **4g**. $F_{||}$ and F_{\perp} are the fluorescence intensities in the direction parallel and perpendicular to the dye molecule.

properties; and fluoro-substituted MLC-2039 which has negative dielectric anisotropic properties. The guest dyes **1**, **4**, **8** and **12** were mixed with the LC host phase, where it was assumed that the dye molecules orient themselves parallel to the LC director. Benzothiadiazole-type dyes **1**, **4**, **8** and **12** are classified as positive dichroic dyes as the direction of their transition moment lies parallel to their molecular axis. It could be demonstrated that, from the polarization spectra both the predominant absorption and fluorescence are in the direction parallel to the molecular axis of **1**, **4**, **8** or **12**. As an example of the positive dichroism found in these dyes, the polarized absorption and fluorescence spectra of **4g** in negative dielectric MLC-2039 is shown in Fig. 3. The dichroic ratios N_A and N_F of **4a** and the parent molecule **1** are summarized in Table 2. The positive dichroic dye, methoxy-substituted **4a**, exhibits high dichroic ratios both in the absorption ($N_A = 7.7$) and the emission spectra ($N_F = 7.7$) in negative dielectric MLC-2039 media, whereas only poor dichroic ratios of 2.0–5.0 in both absorption and fluorescence were found for **1** and **4a** in positive dielectric anisotropy-type LC media.

The effect of the chain length of alkoxy, alkoxymethyl, and carboalkoxy substituents of the dyes on the dichroic ratio N is summarized in Table 3. It can be seen that the N_A and N_F values of **4** become larger for longer alkoxy substituents, with a

Table 3 Dichroic ratios N_A and N_F of **4**, **8** and **12** in liquid crystalline medium MLC-2039^{a,b}

| Compound | N_A | N_F |
|-------------------------|--------|--------|
| 4a ^c | 7.7 | 7.7 |
| 4b ^c | 8.7 | 8.7 |
| 4c | 8.7 | 8.7 |
| 4d | 8.3 | 9.1 |
| 4e | 8.7 | 8.7 |
| 4f | 9.1 | 9.1 |
| 4g | 9.1 | 9.1 |
| 8a | 7.1 | 7.7 |
| 8b | 6.6 | 6.8 |
| 8c | 7.4 | 7.4 |
| 8d | 6.8 | 7.1 |
| 8e | 7.7 | 7.4 |
| 12a ^c | Insol. | Insol. |
| 12b | 5.1 | 8.7 |
| 12c | 6.1 | 8.3 |
| 12d | 6.3 | 8.0 |

^a Excitations of the molecules were done at the wavelength of 350 nm. ^b Concentration of the fluorescent molecules in MLC-2039 is 0.5% (w/w). ^c Concentration of the fluorescent molecules in MLC-2039 is less than 0.5% (w/w).

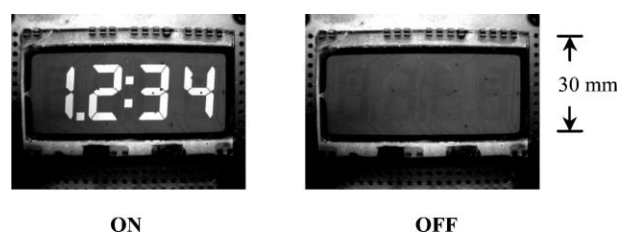


Fig. 4 Reflective LCD model using dichroic fluorescent benzothiadiazole dyes. The host liquid crystalline medium is MLC-2039. The guest dichroic fluorescent dye is a mixture of **4a**–**4g**. The total concentration of the guest dye is 3% (w/w).

saturation at chain lengths C4/C5. This suggests that with these chain lengths, the length of the dye is approaching that of the host MLC-2039. LC cells with **4f** and **4g** as guest dyes exhibit extremely high dichroic ratios, N_A of 9.1 (440 nm) and N_F of 9.1 (540 nm), in the absorption and fluorescence spectra.

In the case of the alkoxymethyl-substituted **8** and diesters **12**, the N_A and N_F values are also high with $N_A \approx 7.7$, and $N_F \approx 7.7$ for **8**, and $N_A \approx 6.3$ and $N_F \approx 8.7$ for **12**. Nevertheless, here the N -values seem to be independent of the length of the alkyl groups. However, the alkyl groups introduced in **4**, **8** and **12** are useful in that they improve the solubility of the molecules in the LC media.

An effective LCD could be fabricated with a mixture of fluorescent dye **4** in MLC-2039 (Fig. 4). Fig. 5 shows the schematic model of this fluorescent host–guest liquid crystal display device. The cell contained a mixture of fluorescent dyes **4** in negative dielectric anisotropy liquid crystal MLC-2039 at a total concentration of 3% (w/w). The indium-tin-oxide (ITO)

Table 2 Dichroic ratios N_A and N_F of **1** and **4a** in different commercial liquid crystals (ZLI-1565, ZLI-4792, E-8, MLC-2039)^a

| Compound | ZLI-1565 | | ZLI-4792 | | E-8 | | MLC-2039 | |
|------------------------|----------|--------|----------|--------|--------|--------|----------|--------|
| | N_A | N_F | N_A | N_F | N_A | N_F | N_A | N_F |
| 1 ^b | 3.6 | 4.3 | 3.8 | 4.8 | 3.2 | 2.2 | 3.6 | 2.8 |
| | — | 492 nm | 421 nm | 490 nm | 426 nm | 500 nm | 424 nm | 487 nm |
| 4a ^c | 4.5 | 4.3 | 4.4 | 5.0 | 4.1 | 3.6 | 7.7 | 7.7 |
| | — | 545 nm | 434 nm | 540 nm | 440 nm | 558 nm | 434 nm | 540 nm |

^a Fluorescence spectra were obtained from the excitation of the molecules at $\lambda = 350$ nm. ^b The concentration of **1** is 0.5% (w/w). ^c The concentration of **4a** is less than 0.5% (w/w) due to the low solubility of the methoxy group.

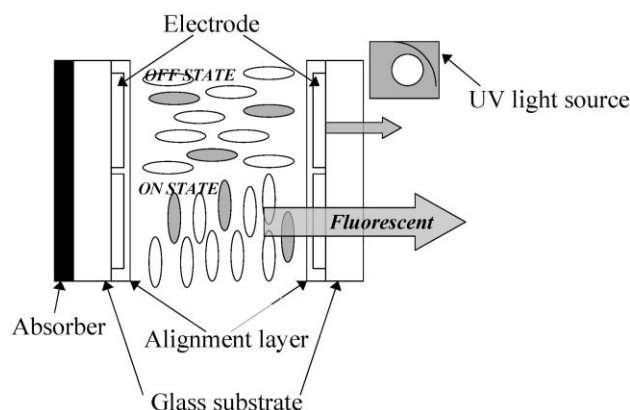


Fig. 5 Schematic model of the fluorescent host-guest liquid crystal display device. The indium-tin-oxide (ITO) electrodes are deposited on the flat surface of the glass plate. The electrode surfaces of the cell are coated with an alignment layer. The cell thickness is 6 μm . The black-light blue fluorescent lamp is used as the front UV light source and the rear absorber is formed as a lacquer.

electrodes were deposited on the flat surface of the glass plate. The electrode surfaces of the cell were coated with an alignment layer in order to induce a homeotropic orientation of the mixture of fluorescent dyes **4** in the host LC. The cell thickness was controlled by using silicon balls of 6 μm diameter. The black-light blue fluorescent lamp was used as the front UV light source and the rear absorber was formed as a lacquer. The LC mixture was aligned perpendicular to the substrate surfaces. Therefore, the rear absorber in non-addressed segments of the display absorbed UV light and they appeared dark (Off-state). The application of an electric field (applied voltage: 10 Vp-p square wave, 60 Hz) between the electrodes resulted in a realignment of the LC mixture molecules perpendicular to the electric field. The fluorescent dyes **4** in the addressed segments of the display absorbed UV light and they emitted fluorescence (On-state).

Conclusions

A number of novel 4,7-bis(*p*-substituted-phenyl)benzo-2,1,3-thiadiazoles **4**, **8**, and **12** have been synthesized. These molecules act as highly fluorescent dichroic dyes in host-guest fluorescent LC displays. The dyes show practical dichroic ratios of $N > 8.0$ and possess good solubility in commercial LC media, without destabilization of the LC phase. The dyes **4**, **8** and **12** exhibit strong fluorescence in the visible region (blue to yellow).

Experimental

General

Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. Infrared spectra were recorded on a JASCO FT/IR-470 plus Fourier Transform Infrared Spectrometer and measured as KBr pellets. ^1H NMR spectra were determined in CDCl_3 , CD_2Cl_2 , or $\text{DMSO}-d_6$ using a JEOL EX-270 spectrometer (270 MHz) and chemical shifts (δ)

are reported in ppm downfield of tetramethylsilane (TMS). The coupling constants (J) are reported in Hz. Mass spectra were recorded with a JEOL JMS-70 mass spectrometer either in EI-mode at 70 eV using a direct inlet system or in FAB-mode with *m*-nitrobenzyl alcohol as the matrix. UV/Vis spectra were measured on a JASCO V-570 spectrophotometer in a 1 cm wide cell. Fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer in a 1 cm wide cell. Analytical TLC was carried out on silica gel coated on aluminium foil (Merck 60 F₂₅₄). Column chromatography was carried out on silica gel (Wako C-300 or KANTO 60N).

Synthesis of materials

Trimethylborate (>97%, TCI), *p*-formylphenylboronic acid (**5**) and $\text{Pd}(\text{PPh}_3)_4$ (TCI) were used as received. The *p*-alkoxyphenylboronic acids **3a–g** were prepared from the corresponding *p*-alkoxyaryl bromides (all TCI) by lithiation and quenching with trimethylborate according to literature procedures.¹¹

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