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INTRAMOLECULAR ENERGY TRANSFER THROUGH LINEAR POLYENES. EFFECT OF SPACERS.

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Abstract *The optical properties of linear polyenes terminally substituted with different molecules (mainly anthryl- and TPP-substituents) have been studied. Bicyclic spacers within the polyene chain affect the quantum yields but do not interrupt intramolecular energy transfer between the endgroups.*

1. INTRODUCTION

In today's molecular chemical physics there is growing interest in investigating not only single organic molecules or the molecular solid state, but supermolecules or molecular functional units with specific physical, chemical or biological functions. On this line of research, we tried to find supermolecules in which energy absorbed in one specific component of the molecule can be transferred to an other one. There is hope that, in future, elements can be designed which perform logical functions on molecular electronic level.

We have already shown¹ that in linear polyene molecules with two different substituents at both ends an intramolecular transfer of energy is possible and detectable. The present paper continues this research. In particular, the quantum yields of the different emissions observed from these supermolecules are determined and the question concerning the role of spacers incorporated into the polyene chain is addressed.

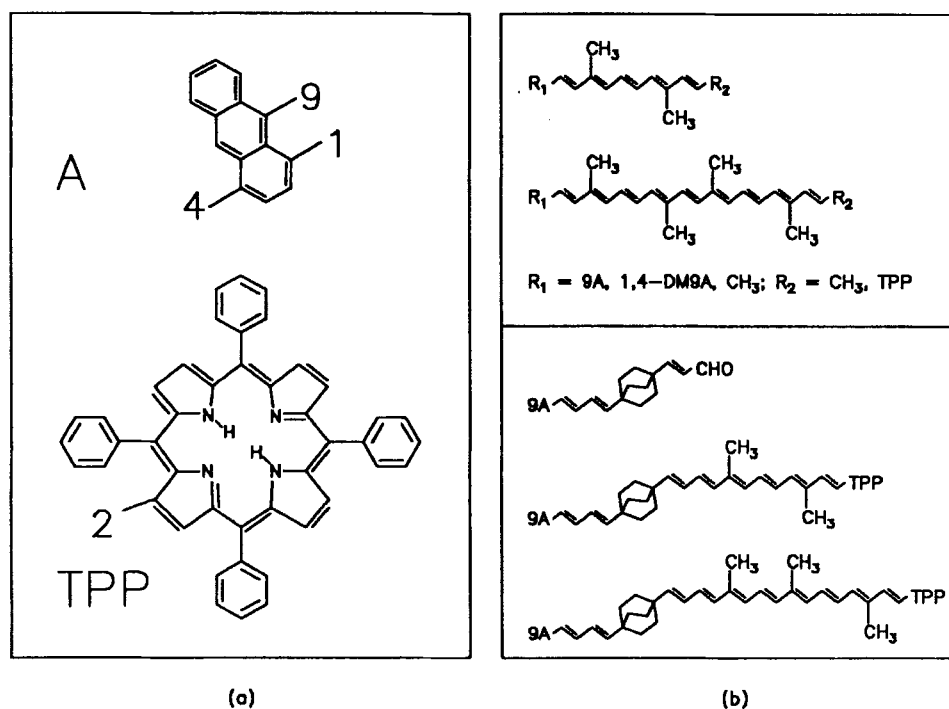


FIGURE 1 Molecular structure of
 (a) the substituents anthracene (A), 1,4-dimethyl-anthracene (DMA),
 tetraphenylporphyrin (TPP) and of
 (b) the supermolecules $R_1-P_n-R_2$ ($n=5$ or 9), $9A-P_2-Bic-P_1-CHO$,
 $9A-P_2-Bic-P_n-TPP$ ($n=6$ or 8).

2. EXPERIMENTAL

We have studied the optical properties of two types of supermolecules consisting of linear polyene chains terminally substituted with different molecules (mainly anthracenes and tetraphenylporphyrin).

The first type (same as studied before^{1,2}) contains a single polyene chain stabilized by methyl side groups in linear configuration. The second type additionally contains a spacer molecule, bicyclo[2.2.2]octane ("Bic"), which interrupts the conjugated polyene chain but does not absorb or emit light in the spectral regions of interest. Keeping within the schemes indicated in Fig. 1 the

following nomenclature for the different molecules is used throughout this paper: A-P_n-TPP for polyene chains containing n double bonds (n=5 or 9) without spacer and A-P₂-Bic-P_n-TPP for molecules with spacer (Bic), differing in chain length on the TPP-substituted side (n=6 or 8).

The molecules usually were dissolved in n-hexane, in case of low solubility in chloroform (absorption spectrum of H₃C-P₉-TPP in Fig. 2(a)). The concentrations used were below $5 \cdot 10^{-6}$ mole/l in order to avoid concentration effects and to maintain low optical densities. The solutions were degassed from oxygen by repeated freeze-and-thaw cycles.

Optical spectra were measured by standard techniques, absorption at 295K, emission and excitation at 180K, while staying above the solidification temperature of the solvent. Emission spectra were corrected with respect to the spectral sensitivity of the detection system, excitation spectra were normalized to equal numbers of exciting photons. Quantum yields were measured relative to common standards: anthracene in n-hexane (30%)³, perylene in cyclohexane (78%)⁴ and TPP in benzene (11%)⁵.

3. MOLECULES WITHOUT SPACER

The absorption spectrum of the molecule 9A-P₉-TPP is shown in Fig. 2(a) in comparison with those of the reference molecules H₃C-P₉-TPP and 9A-P₉-CH₃, respectively, and of the substituents anthracene and TPP. The spectrum clearly exhibits features characteristic for all three partner molecules: the S₃+S₀ anthryl absorption at about 256nm, the S₂+S₀ and S₁+S₀ TPP absorption (B- and Q-bands, respectively) with its most prominent maximum at about 425nm (B_x^{0,0}) and the S₂+S₀ polyene (P₉) absorption contributing shoulders on both sides of the main TPP band. With respect to the individual molecules a loss of structural details and a slight red-shift is observed generally. While the extinction coefficients of the main A and TPP bands are strongly reduced, increasing absorption is observed in the spectral regions of TPP Q-bands and polyene. Both of these effects must be due to coupling between the substituent molecules and the polyene, which is more distinct for TPP substitution according to Fig. 2(a) (spectra of the reference molecules). Qualitatively the same behaviour is found for the corresponding compounds with shorter chain length (P₅) and for DMA substitution. The P₅ absorption is decreased in strength relative to P₉ and blue-shifted, the absorption with DMA substituents is comparable to molecules with 9A substituents.

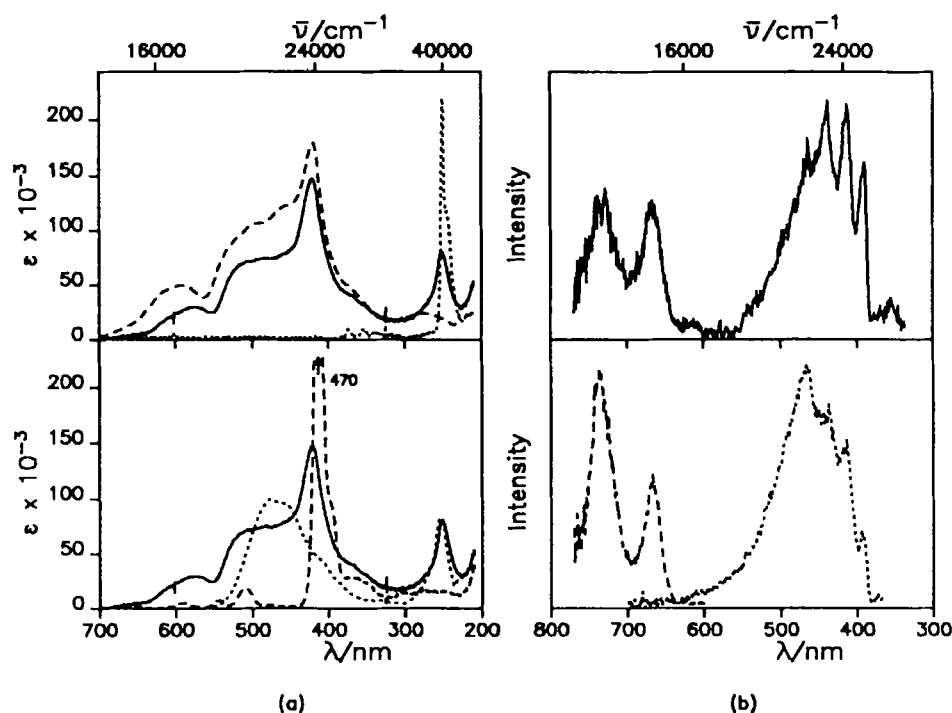


FIGURE 2

(a) Absorption spectra

top: — 9A-P₉-TPP, - - - H₃C-P₉-TPP, A
 bottom: — 9A-P₉-TPP, 9A-P₉-CH₃, - - - TPP

(b) Emission spectra

top: — 9A-P₉-TPP,
 bottom: - - - H₃C-P₉-TPP, 9A-P₉-CH₃

Examples for the fluorescence emission spectra of 9A-P₉-TPP, 9A-P₉-CH₃ and H₃C-P₉-TPP are given in Fig. 2(b). All spectra were obtained during excitation at $\lambda_{\text{exc}} = 256\text{nm}$ and normalized to the same maximum intensity. Dual, blue and red, fluorescence emissions are observed from the supermolecule, but single, blue or red, fluorescence components from the reference molecules. However, the respective emissions show the same spectral features, are located in the anthracene and TPP fluorescence regions (for $S_1 \rightarrow S_0$ transitions) and therefore are clearly determined by the substituents. Remarkably, in the 9A-P₉-CH₃ reference molecule the A-like fluorescence is maintained whereas in 9A-P₈-CHO

it is totally quenched⁶. The relative intensity of red versus blue emission in the supermolecule is increased at shorter chain length (P_5) and also with excitation at longer wavelength (due to more direct TPP excitation, cf. Fig. 2(a)).

A quantitative evaluation of the fluorescence quantum yields was performed for blue and red emissions of the different compounds. Values obtained during excitation at $\lambda_{\text{exc}} = 256\text{nm}$ are summarized in Table 1. In general they are very low in the composite molecules. Compared to the single substituent molecules the quantum yield of the blue emission is more heavily reduced for short than for long polyene chains. Red emission quantum yields are higher with DMA than with A substituents, blue emission quantum yields are lower.

Table 1 Quantum yields in %, measured for $\lambda_{\text{exc}} = 256\text{nm}$. The given values belong to the red and blue emissions of the molecules, respectively. The experimental errors are within $\pm 20\%$.

molecule	red emission	blue emission
A	-----	45
1,4DMA	-----	31
TPP	1.6	-----
H ₃ C-P ₅ -TPP	0.9	-----
9A-P ₅ -TPP	0.1	0.4
1,4DM9A-P ₅ -TPP	0.2	0.2
H ₃ C-P ₉ -TPP	0.2	-----
9A-P ₉ -TPP	0.03	1.7
1,4DM9A-P ₉ -TPP	0.2	0.4
9A-P ₂ -Bic-P ₁ -CHO	-----	49
OHC-P ₆ -TPP	0.4	-----
9A-P ₂ -Bic-P ₆ -TPP	1.7	9
OHC-P ₈ -TPP	0.2	-----
9A-P ₂ -Bic-P ₈ -TPP	0.1	3

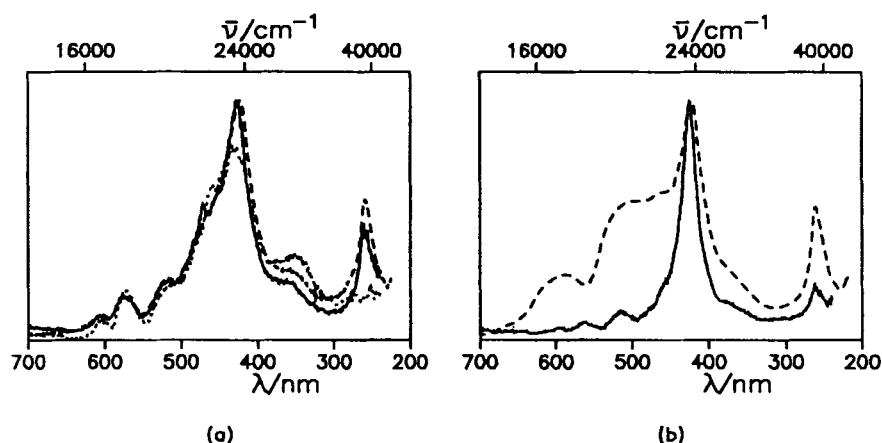


FIGURE 3 Excitation and absorption spectra

- (a) ——— excitation of 1,4-DM9A-P₅-TPP ($\lambda_d = 730\text{nm}$),
 - - - absorption of 1,4-DM9A-P₅-TPP,
 excitation of H₃C-P₅-TPP ($\lambda_d = 730\text{nm}$)
 (b) ——— excitation of 1,4-DM9A-P₉-TPP ($\lambda_d = 730\text{nm}$),
 - - - absorption of 1,4-DM9A-P₉-TPP

Excitation spectra have been measured with selective detection of the red (TPP) emission at $\lambda_d = 730\text{nm}$. Examples are given in Fig. 3 for the molecules 1,4-DM9A-P₅-TPP and 1,4-DM9A-P₉-TPP together with the corresponding absorption spectra. In the case of the shorter chain length the excitation spectrum follows the features of the absorption spectrum quite well. Apparently the TPP-emission is strongly excited not only in the spectral regions being typical for TPP absorption but also in all other regions, particularly in that of anthracene ($S_3 \leftarrow S_0$) absorption. This excitation band is missing (Fig. 3(a)) for H₃C-P₅-TPP, a compound without A-substituent. Our results provide important evidence for an energy transfer within the supermolecule, which was already discussed in the literature¹.

A distinct difference between excitation and absorption spectra is observed at $\lambda > 425\text{nm}$, below the TPP B-Band, for the molecule with longer chain length. Such excitation is not effective for populating the TPP S_1 -state that the emission emerges from. Consequently the coupling between polyene and TPP in that energy region must be strongly dependent on chain length. On the other hand energy transfer from anthracene to TPP is still possible, even though the A S_3 -band of the excitation spectrum in Fig. 3(b) has reduced intensity with respect to Fig. 3(a).

4. MOLECULES WITH SPACER

In Fig. 4 the absorption spectra of the supermolecules with spacer $9A-P_2-Bic-P_n-TPP$ ($n=6$ or 8) are compared with those of the corresponding reference molecules, $9A-P_2-Bic-P_1-CHO$ and $OHC-P_n-TPP$ ($n=6$ or 8). The synthetic spectra are constructed by normalizing the component spectra at the A S_3 -band and the TPP Q-bands, respectively. With respect to the supermolecules without spacer the essential spectroscopic features are maintained and determined by the partner molecules anthracene, polyene (P_6 , P_8) and TPP . Similarly the shoulders in the polyene spectral region are red-shifted for the P_8 relative to the P_6 compound. Moreover, additional distinct bands at 220nm, 280nm and 290nm appear in the spectra of both reference and supermolecules.

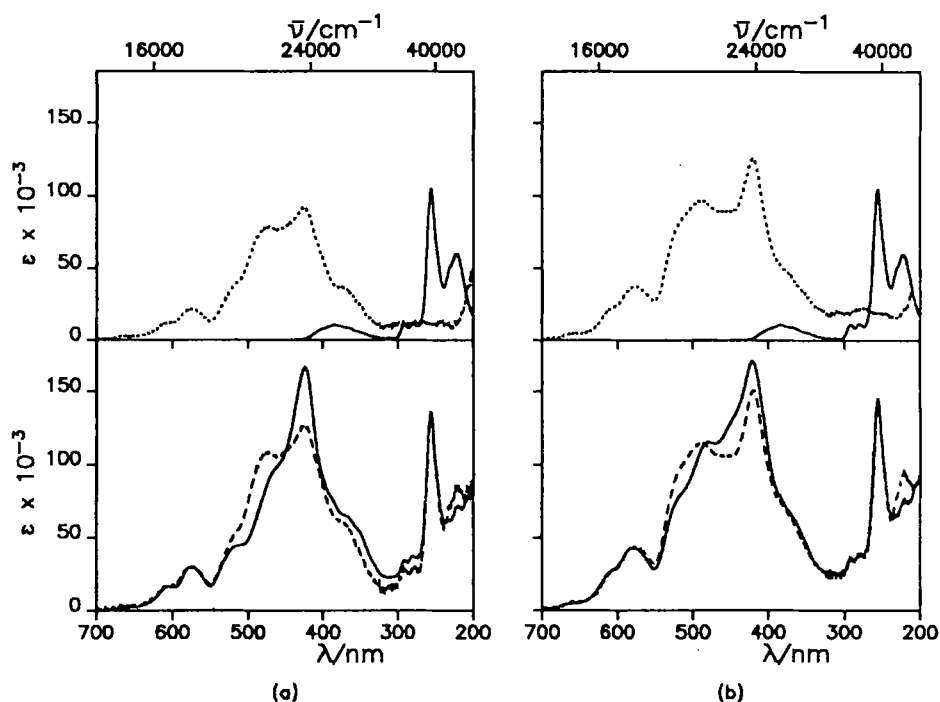


FIGURE 4 Absorption spectra of molecules with spacer

- (a) top: — $9A-P_2-Bic-P_1-CHO$, - - - $OHC-P_6-TPP$
 bottom: — $9A-P_2-Bic-P_6-TPP$ measured, - - - synthetic (see text)
 (b) top: — $9A-P_2-Bic-P_1-CHO$, - - - $OHC-P_8-TPP$
 bottom: — $9A-P_2-Bic-P_8-TPP$ measured, - - - synthetic (see text)

Whereas the 220nm band can be attributed to the short polyene chains and the CHO-group, the other two bands probably are due to mixed states originating from coupling between anthracene and polyene P_2 . The comparative results of Fig. 4 provide no indication for coupling between the polyene partners P_2 and P_n across the spacer within the supermolecules.

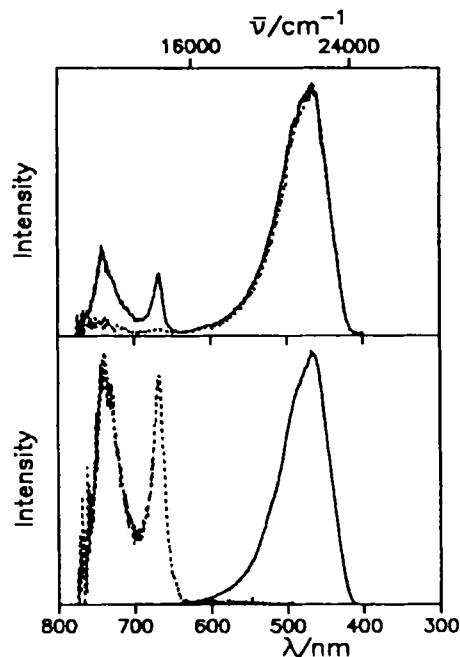


FIGURE 5 Emission spectra of molecules with spacer
top: — 9A- P_2 -Bic- P_6 -TPP, 9A- P_2 -Bic- P_8 -TPP
bottom: — 9A- P_2 -Bic- P_1 -CHO, OHC- P_6 -TPP

Examples for the fluorescence emission spectra of the same supermolecules and reference molecules as above are compiled in Fig. 5. All spectra were obtained during excitation at $\lambda_{\text{exc}} = 256\text{nm}$ and normalized to the same maximum intensity. As in section 3 dual fluorescence emissions, blue and red, are observed from the supermolecule, single blue or red emissions from the reference molecules. In contrast to Fig. 2(b) the blue emission is further red-shifted and has completely lost its vibronic sub-structure. Variation of the polyene P_n chain length does not affect band positions and shapes, but the relative intensity of the red emission in the spectra is higher for P_6 - than for P_8 -compounds.

A quantitative evaluation of the fluorescence quantum yields of different compounds with spacer was performed in the same manner as in section 3, for blue and red emissions with $\lambda_{\text{exc}} = 256\text{nm}$. The obtained values listed in Tab. 1 (see section 3) show distinct variations in absolute numbers. Whereas for 9A-P₂-Bic-P₁-CHO the observed quantum yield of blue emission is as high as for the anthracene molecule, it is decreased for the supermolecule. The reduction is stronger for the P₈- than for the P₆-compound with spacer, but still essentially smaller than for supermolecules without spacer. The quantum yield of the red emission is about four times smaller for OHC-P₆-TPP than for the TPP molecule and about as high as in TPP for the P₆-supermolecule. In the supermolecule and reference molecule with P₈, however, the quantum yield is drastically reduced and comparable to those of corresponding molecules without spacer.

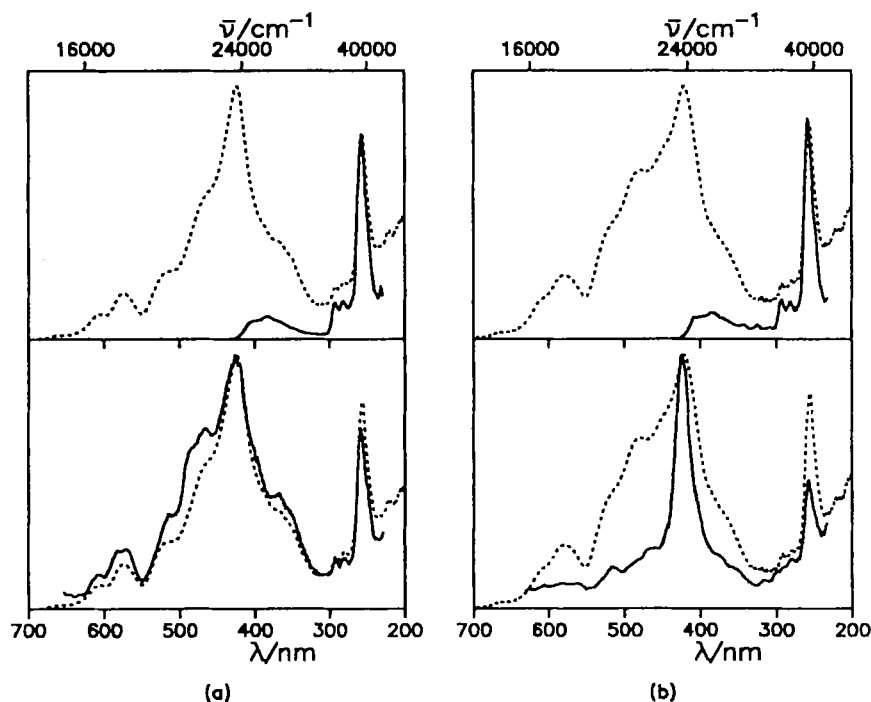


FIGURE 6 Excitation spectra of molecules with spacer in comparison with absorption spectra

(a) 9A-P₂-Bic-P₆-TPP

top: absorption, — excitation ($\lambda_d = 466.5\text{nm}$)

bottom: absorption, — excitation ($\lambda_d = 667.5\text{nm}$)

(b) 9A-P₂-Bic-P₈-TPP

top: absorption, — excitation ($\lambda_d = 466.5\text{nm}$)

bottom: absorption, — excitation ($\lambda_d = 663.5\text{nm}$)

Excitation spectra of the supermolecules 9A-P₂-Bic-P₆-TPP and 9A-P₂-Bic-P₈-TPP have been measured with selective detection on red and blue emission (red at $\lambda_d = 667.5\text{nm}$ and 663.5nm , respectively, blue for both molecules at $\lambda_d = 466.5\text{nm}$). In Fig. 6 they are compared with the corresponding absorption spectra. The excitation spectra of both molecules completely reflect the structure of the absorption spectrum of the reference molecule 9A-P₂-Bic-P₁-CHO (Fig. 4 top) when detected in the blue spectral region. On the other hand, in case of red light detection for only the P₆-compound the excitation spectrum follows all relevant features of the absorption. Similar to the case without spacer (Fig. 3) the excitation spectrum of the P₈-compound is strongly narrowed in the polyene absorption regions. The specific A-S₃ absorption band is preserved for both supermolecules, carrying less contribution for the longer chain in agreement with the observations in section 3. The observed spectroscopic results provide evidence for existing intramolecular energy transfer between the endgroups of the supermolecules with spacer (with energy flow from the anthracene to the TPP side).

5. CONCLUSION

Comparative studies on optical spectra and quantum yields of substituted polyenes with and without spacers have been performed. In molecules without spacer only a small fraction of the excitation energy is emitted radiatively. When introducing a bicyclic spacer, the fluorescence quantum yields are enhanced and intramolecular transfer of energy from the A- to the TPP-endgroup is still observed.

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