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Effect of wave-function delocalization on the exciton splitting in organic conjugated materials

M. Muccini,[1,*] M. Schneider,[1] C. Taliani,[1] M. Sokolowski,[2] E. Umbach,[2] D. Beljonne,[3] J. Cornil,[3] and J. L. Brédas[3]
[1]Istituto di Spettroscopia Molecolare, CNR, via Gobetti 101, 40129 Bologna, Italy
[2]Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
[3]Service de Chimie des Materiaux Nouveaux, Université de Mons-Hainaut, 20 Place du Parc, B-7000 Mons, Belgium

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Interchain interactions in organic conjugated solids causes a splitting of the lowest excited electronic states which depends on the relative packing of the chromophores and on the conjugation length. The splitting (also known as Davydov splitting) was measured for the first time in a model compound (α-sexithienyl), but the question remained open on how the Davydov splitting depends on the conjugation length. This question is particularly important because the relative location of the excitonic components plays a major role in determining the photophysics of the systems. We have therefore measured the Davydov splitting of the lowest $1\,^1B_u$ exciton in the model systems of α-quaterthienyl (T_4) and α-sexithienyl (T_6) from the low-temperature polarized absorption of oriented single crystals. Due to the very similar crystal structure of the two materials, the change in exciton splitting can be directly related to the different molecular wave-function delocalization over the chain. Here we show that the Davydov splitting of the lowest exciton decreases as the molecular wave-function delocalization increases. This result, which contradicts the dipole model expectations, is confirmed by correlated quantum-chemical calculations. In addition, we predict the size of the interchain interactions in the polymer where a direct optical measurement is precluded by the intrinsic molecular disorder.

I. INTRODUCTION

Organic conjugated materials have been intensively investigated in recent years with the perspective of a new generation of flat panel electroluminescent displays[1,2] and thin-film electronics.[3–5] Despite the significant improvement in prototype device performance, the detailed understanding of the basic phenomena determining device operation is still a matter of debate and definitively deserves further investigation. In particular, the different charge transport and luminescent properties with respect to conventional semiconductors, are to be considered in view of the peculiar intermolecular interactions in the solid. The specific van der Waals interactions cause the formation of an exciton band and a splitting of the molecular electronic state into as many components as the number of molecules in the unit cell (Davydov components)[6] whose energy depend on the molecular electronic properties and on the crystal packing. Due to momentum conservation, radiative emission occurs at wave vector close to zero ($K \sim 0$) at the bottom of the exciton band and the transition probability depends on the character of the lowest excitonic Davydov component. If the lowest component is dipole forbidden, emission is suppressed and is conversely strong if the lowest component is allowed. It is therefore crucial to understand the effect of the conjugation length on the size of the Davydov splitting in order to understand the luminescent properties of conjugated materials. Similarly, the intrinsic intermolecular interactions have a direct impact on the charge transport properties determining the electronic structure of the material, and the characteristics of the neutral and charged excitations. Nevertheless, there are still open questions concerning the effect of the molecular wave-function delocalization on the exciton structure. In the case of weak interactions (when the wave functions of the molecules in the solid are assumed to be unaffected by the intermolecular forces) the dipole approximation of the exciton model has proven to be valid.[7] The Davydov splitting in this case is predicted to increase[8] for increasing chain length. In the strong interaction limit (when the molecular wave-function is not localized onto a single chain) calculations need to be based on delocalized wave-functions and the exciton theory fails. Correlated quantum-chemical calculations for the strong interaction case indicate that intermolecular interactions within a molecular aggregate decrease with conjugation length and eventually vanish for chains of infinite size.[9–11] However, up to date there are no experimental data available showing either the size or the trend of the wave-function delocalization effect on the exciton splitting in organic conjugated materials.

Among conjugated systems, oligothienyls are considered good models for the electronic structure and the photophysics of a wider class of conjugated materials, and have potential direct applications in optoelectronic devices such as thin-film transistors.[3–5] Recently, we gave the experimental evidence of the extent of the exciton splitting in organic conjugated systems by measuring the Davydov splitting of the lowest $1B_u$ singlet exciton from the optical absorption of solid T_6.[12]

In this paper, we show the effect of molecular wave-function delocalization on the exciton structure in organic conjugated materials, and demonstrate by a joint experimental and theoretical work that the exciton splitting decreases as wavefunctions are more delocalized over the chain. The delocalization overwhelms the slightly decreasing interchain distance in longer chain materials. Furthermore, we predict the size of the exciton splitting in real polythienyl by simulating the Davydov splitting of the lowest singlet exciton of α-octithienyl (T_8).

II. EXPERIMENT

The T_4 and T_6 single crystals used for the low-temperature polarized absorption experiments were grown by sublimation as described in detail elsewhere.[13] Single crystals grow as self-sustaining plates a few millimeters long with thickness of the order of 10 microns. The flat surface of the single crystals corresponds to the *bc* plane, as shown by x-ray diffraction analysis.[13] The samples were oriented under a polarizing microscope before they were mounted in the sample holder of a helium bath cryostat. The absorption spectra were measured at 4.2 K with a spectrophotometer allowing a resolution of 5 cm^{-1} over the entire spectral range. The light was propagating along the *a* crystal axis and was polarized parallel to the *b* or *c* crystal axes before impinging the sample. Both the sample and the reference signal were detected by a photomultiplier.

III. RESULTS AND DISCUSSION

The crystal structure of sublimed T_4 and T_6 single crystals[14,13] that we have examined is reported in Fig. 1. The molecular electronic states transform according to the irreducible representation of the C_{2h} point group. The crystal system is monoclinic and the space group is $P2_1/a$, $P2_1/c$, or $P2_1/n$, depending on the alternative cell choice. The four molecules in the unit cell pack according to the typical herringbone structure and are aligned strictly parallel to each other, with the intermolecular distance within a single *bc* layer being much shorter than that between different layers.

The lowest electronic excited state of the T_6 molecule is $1\,{}^1B_u$.[15,16] In the solid it has been shown to be polarized along the long molecular axis (*L*),[17,18] while the $2\,{}^1B_u$ is polarized along the short in-plane molecular axis (*M*)[17] (see Fig. 1). The crystalline field induces the splitting of the lowest ${}^1B_u$ molecular excited state into four crystalline states of a_g, a_u, b_g, and b_u symmetry within the C_{2h} point group.[19] The layered crystal structure (Fig. 1) leads to the nearly degeneracy of the homologous *gerade* and *ungerade* crystal levels, as confirmed by the qualitative results of the $K=0$ point-dipole exciton model,[19] which also predicts the *b*-polarized a_u level to be at lower energy. The other optically accessible Davydov component (b_u) is at higher energy and polarized in the *ac* crystal plane. The energy difference between the one-photon allowed Davydov components (a_u and b_u) gives the Davydov splitting of the corresponding exciton due to the intermolecular interactions in the solid. The same analysis applies for T_4. The Davydov splitting of the lowest singlet exciton ($1\,{}^1B_u$) can be directly measured from the low temperature polarized absorption of oriented single crystals.

Figure 2 shows the low temperature *b*- and *c*-polarized absorption spectra of T_4 and T_6 single crystals. In both materials, the lowest energy transition is strongly *b* polarized consistent with the a_u Davydov component. Therefore, we assign the bands at 21 080 cm^{-1} in T_4 and at 18 360 cm^{-1} in T_6 to the lowest a_u Davydov level. As reported in details elsewhere,[12] the Herzberg-Teller mechanism[20] is active in coupling the a_u electronic origin with totally symmetric modes. The absorption spectra of T_4 and T_6 become more *c* polarized as the energy increases. This is due to the Herzberg-Teller coupling between the $1\,{}^1B_u(\|L)$ and the higher $2\,{}^1B_u(\|M)$ states via totally symmetric modes. As a result, the vibronic transition moment is rotated toward the polarization direction of the lending state $2\,{}^1B_u(\|M)$, which is expected to be *c* polarized.[19] The detailed description of the vibronic assignment of the T_4 polarized absorption spectra is reported in Table I, and is in good agreement with previous results on matrix isolated T_4.[15]

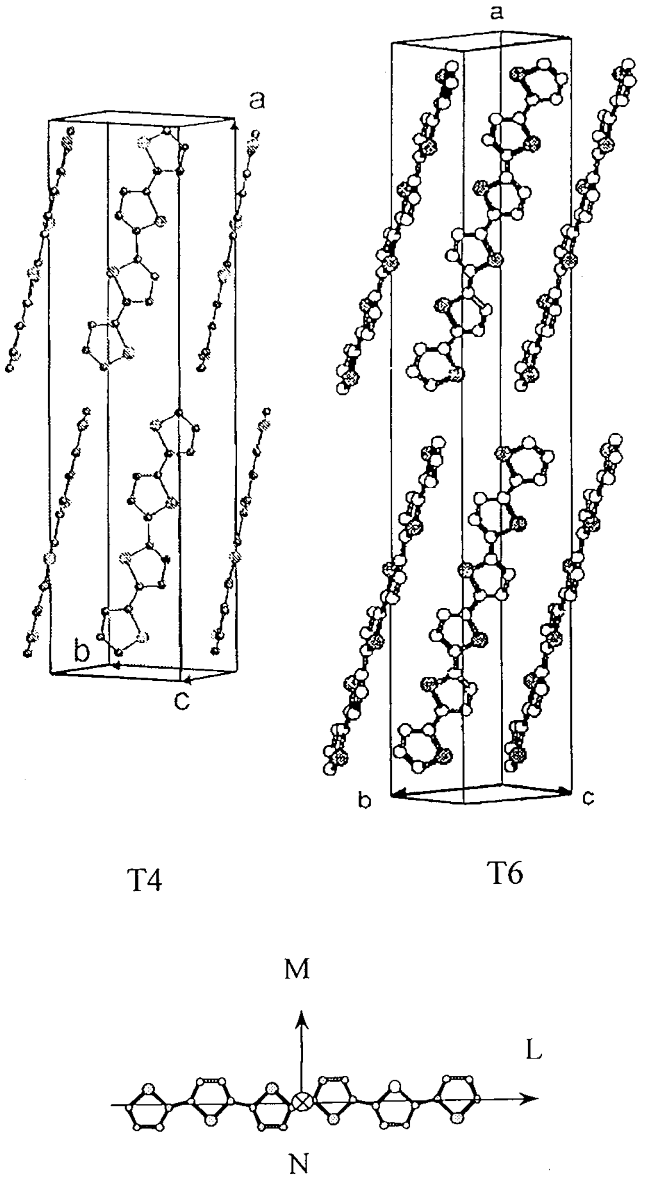

FIG. 1. Crystal structure of the low temperature phase of T_4 and T_6. The *a*, *b*, and *c* crystal axes as well as the *L*, *M*, and *N* molecular axes are shown. Note the close similarity of both structures. The arrangement of the four molecules within the unit cell is also representative of the crystal structure of T_8. The herringbone angle is in all cases of 65°–66°.

The intense b_u Davydov component is polarized in the *ac* crystal plane. In order to measure it directly, the *c*-polarized absorption spectra should be measured for energies higher than 24 000 cm^{-1} in T_4 and higher than 21 000 cm^{-1} in T_6. However, the thickness of the samples (of the order of 10 μm) leads to saturation in the *c*-polarized spectrum of T_6. In the case of T_4, the b_u Davydov component can be identified in the *c*-polarized spectrum, although any other features at higher energy are smeared out. Both in T_4 and T_6, the b_u Davydov components are observed in the *b*-polarized spectrum at 23 956 and 20 945 cm^{-1}, respectively, due to an op-

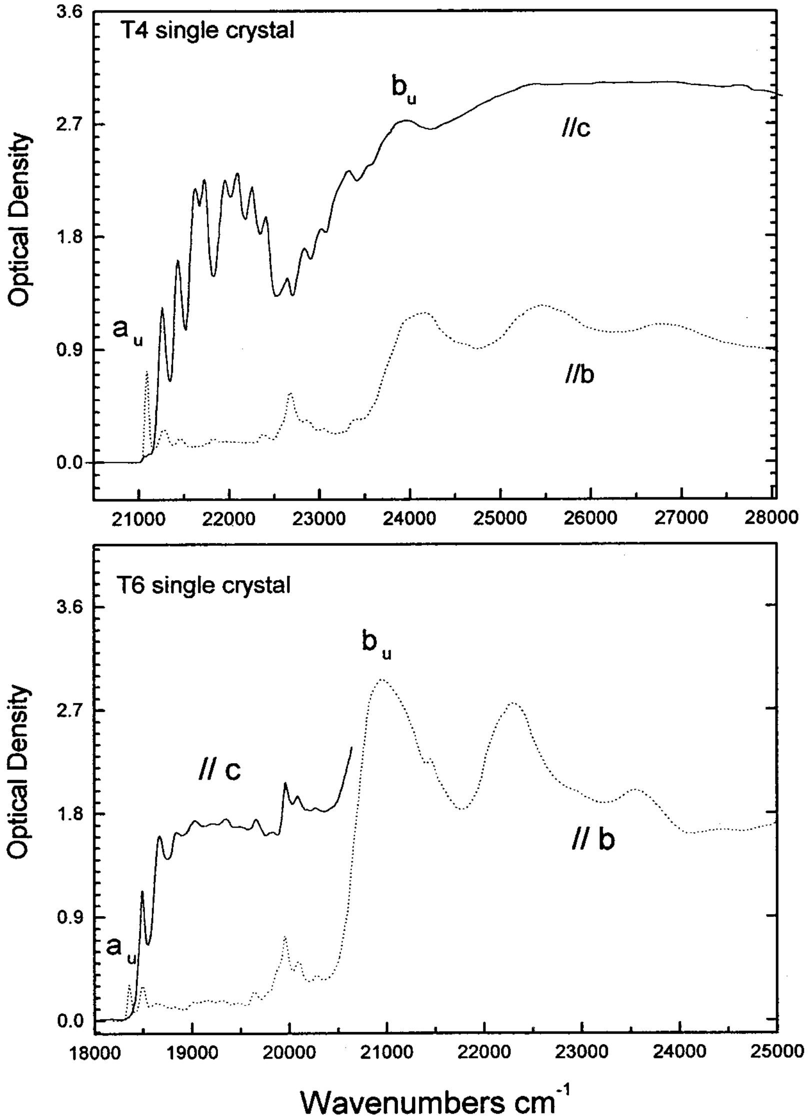

FIG. 2. Top: polarized absorption spectra of T_4 single crystal at 4.2 K along the *b* and *c* crystal axes. The assignment of the vibronic resonances is reported in Table I and discussed in the text. Bottom: polarized absorption spectra of T_6 single crystal at 4.2 K along the *b* and *c* crystal axes. In both cases the two optically allowed Davydov components (a_u and b_u) are indicated.

tical misalignment of the samples. The corresponding Davydov splitting is about 2900 cm^{-1} (0.3 eV) in T_4 and about 2600 cm^{-1} (0.32 eV) in T_6, despite the very similar crystal structure of the two materials and a slightly shorter interchain distance in $T_6\,(4.967\,\text{Å})$[13] with respect to $T_4\,(5.008\,\text{Å})$.[14] We attribute the smaller exciton splitting in T_6 with respect to T_4, to the higher delocalization of the $1\,^1B_u$ molecular wave function over the full length of the six-ring chain. The result demonstrates that the change in wave-function delocalization has a sizable effect on the exciton structure. Moreover, we quantitatively show that a change in the molecule van der Waals length from 14 Å (T_4) to 22 Å (T_6), makes the exciton splitting decreasing of about 10%.

In order to model the singlet electronic excited states in $T_n\,(n=4,6,8)$ clusters, we have combined the semiempirical Hartree-Fock intermediate neglect of differential overlap (INDO) technique to a single configuration interaction (SCI) scheme. We stress that such a technique is size consistent and should thus correctly reproduce the evolution with chain length of the excitation energies. The ground-state geometries are taken directly from the x-ray crystal structures of T_4,[14] T_6,[13] and T_8.[21] Since interchain interactions within the *bc* layers are much stronger than along the *a* axis, we have only considered conjugated chains lying within the same *bc* layer.

In Fig. 3, we show the evolution with cluster size of the INDO/SCI computed Davydov splitting of the $1\,^1B_u$ exciton for T_4, T_6, and T_8. In all cases the Davydov splitting evolves with the number of molecules in the clusters and converges towards its saturated value for about six conjugated chains. To a good approximation, the excitation energies calculated for the largest clusters can be considered to be representative of the crystals.

The most relevant feature is that the quantum-chemical calculations predict a decrease of the Davydov splitting with increasing chain length, which is fully consistent with the spectroscopic observations. We already discussed this effect as due to the increased delocalization over the chain of the $1B_u$ molecular wave function. Figure 4 shows the INDO/SCI-computed two-particle (one hole-one electron) wave functions for the $1B_u$ excited state in the isolated chains of T_4, T_6, and T_8. In oligomers up to T_8, the $1B_u$ wave function does extend over the entire chain, which is consistent with the significant decrease in Davydov splitting when going from T_4 to T_8, despite the unchanged crystal structure and the slightly decreasing interchain distance.

The polarization of the two Davydov components is well

TABLE I. Vibrational assignment of the *b*- and *c*-polarized absorption spectra of T_4 single crystal at 4.2 K. O^{I}, O^{II}, and O^{III} are three false origins due to the coupling of the electronic origin a_u with totally symmetric modes of 168, 342, and 636 cm^{-1} frequency, respectively.

	Polarization *b* origin	Polarization *c* false origins		
cm^{-1}	O a_u	O^{I} 168 cm^{-1}	O^{II} 342 cm^{-1}	O^{III} 636 cm^{-1}
21080	O			
21248	O+168 (−)	O^{I}		
21422	O+2×168 (+6)		O^{II}	
21613		$O^{I}+342$ (+23)		
21716				O^{III}
21767				
21944				
22076				$O^{III}+342$ (+18)
22241				
22376	O+1296 (−)			
22399				
22636				
22670	O+1590 (−)			
22823		$O^{I}+1590$ (−9)		
22838	O+1590+168 (−)			
23015			$O^{II}+1590$ (+3)	
23016	O+1590+2×168 (+18)			
23169				
23307				$O^{III}+1590$ (+1)
23348				
23518				
23956	b_u			
25472				
26817				

reproduced by the calculations, see Table II. The transition energies have been calculated in the ground-state geometry and, therefore, correspond to *vertical* processes. In the case of T_6,[12] we have shown that a good agreement with the measured optical absorption spectrum can be obtained by considering in the theoretical simulations (i) a relaxation energy of about 1000 cm^{-1} for the b_u Davydov component, which is characterized by an intense Franck-Condon activity and (ii) a vanishingly small relaxation energy for the a_u Davydov component, which shows dominant Herzberg-Teller coupling. By applying the same approximation for T_4, 0-0 transition energies in close match with the experimental values are obtained. One should keep in mind, however, that rather drastic approximations have been considered in the theoretical model, on the one hand in the description of the excited-states electronic structure and on the other hand in the handling of the geometric relaxation phenomena. We might thus expect changes in the quantitative values reported in this paper upon more elaborate treatment of the interchain effects. Although the calculated trend of the Davydov splitting has general validity, the good *quantitative* agreement in Table II might thus be accidental; more work is definitively required to assess this issue.

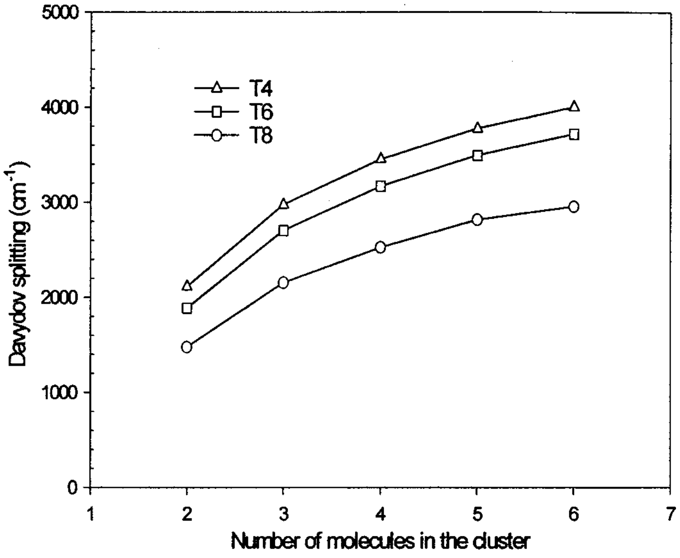

FIG. 3. INDO/SCI computed evolution of the Davydov splitting in T_4, T_6, and T_8 with the number of molecules in the clusters.

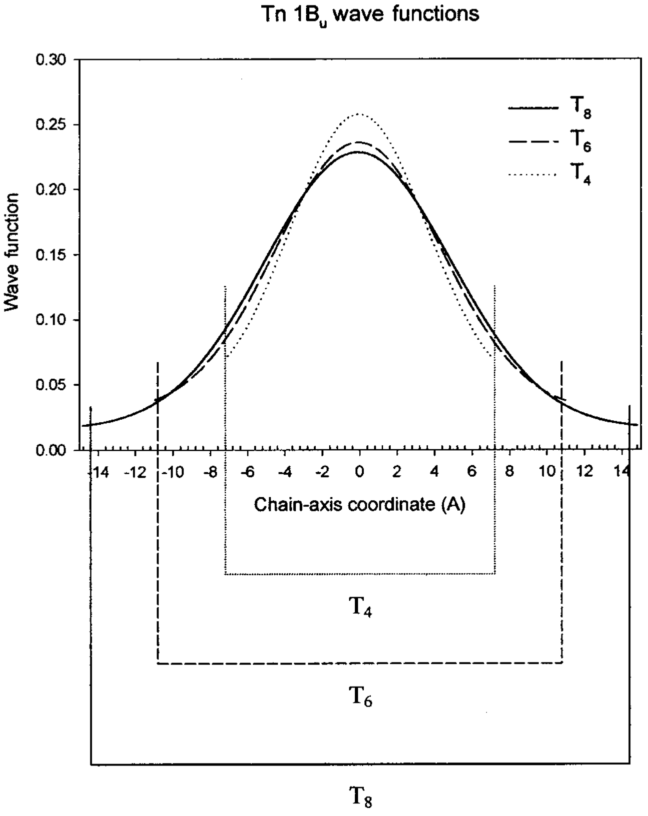

FIG. 4. Spatial delocalization of the $1B_u$ wave functions in the isolated chains of T_4, T_6, and T_8. The computational procedure is described in the text.

TABLE II. Comparison of the measured and calculated energies of the a_u and b_u Davydov components in T_4 and T_6 single crystals. The calculations refer to clusters of six molecules lying within the same bc layer, which are built on the basis of the x-ray crystal structures. Both the vertical (calculated on the basis of the ground-state geometry) and relaxed (obtained by subtracting from the vertical excitation energies relaxation energies of 1000 [0] cm^{-1} for the b_u [a_u] Davydov component, see text) computed transition energies are shown.

	experimental cm^{-1}	calculations cm^{-1}		assignment
		vertical	relaxed	
T_4	21080	21450	21450	$a_u(b)$
	23956	25450	24450	$b_u(ac)$
T_6	18360	18175	18175	$a_u(b)$
	20945	21890	20890	$b_u(ac)$

The Davydov splitting in T_8 six-chain clusters, which can be considered as representative of the exciton splitting in the polymer, is predicted to further decrease with respect to the shorter oligomers as a consequence of the more extended molecular wave function. In the polymer, when considering the same assumptions for the relaxation energies of the two Davydov components, we predict a Davydov splitting of about 2000 cm^{-1} (0.25 eV). We note that the intermolecular distance decreases progressively (of about 0.04 Å) when going from T_4 to T_6 to T_8.[14,13,21] Nevertheless, the effect of the wave-function delocalization dominates over the decreased intermolecular distances, leading to a smaller Davydov splitting.

IV. CONCLUSIONS

In conclusion, we measured the effect of molecular wave-function delocalization on the exciton structure in organic conjugated model systems. In particular, we showed that the exciton splitting is inversely dependent on the molecular wave-function delocalization over the chain. More quantitatively, we measured a 10% decrease in the exciton splitting when going from T_4 to T_6. The experimental results are in agreement with the results of correlated quantum chemical calculations, which also allows us to predict the extent of the exciton splitting in real polymer chains. The results of this paper provides insight into the electronic structure of organic conjugated materials, and have direct implications for the understanding of the optical properties of conjugated polymers.

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*Corresponding author. Email address: muccini@area.bo.cnr.it

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