ISSN 1070-4272, Russian Journal of Applied Chemistry, 2013, Vol. 86, No. 11, pp. 1663−1669. © Pleiades Publishing, Ltd., 2013.
Original English Text © Yu.G. Vlasov, A.A. Kruchinin, D.S. Ryabukhin, 2013, published in Zhurnal Prikladnoi Khimii, 2013, Vol. 86, No. 11, pp. 1711−1717.

## PHYSICOCHEMICAL INVESTIGATION OF SYSTEMS AND PROCESSES

# Fluorescence Quenching Features in Non-Conjugated Diacetylene Oligomers

**Yu. G. Vlasov, A. A. Kruchinin, and D. S. Ryabukhin**

*St. Petersburg State University, St. Petersburg, Russia*
*e-mail: akr@pobox.spbu.ru*

Received November 15, 2013

**Abstract**—It was found that, in diacetylene oligomers constisred of monomer units with an non-conjugated system of π-electrons, the efficiency of fluorescence quenching depends on the chain length within the range from 2 to 40 repeating units. This effect is consistent with the model of propagation of delocalized excitons in a noncovalent aggregate of several oligomer chains. The result obtained in the study confirms the assumption that a collective effect due to excitons can exist in a supramolecular aggregate of non-conjugated molecules.

**DOI:** 10.1134/S1070427213110062

In recent years, considerable attention was paid to syntheses and studies of organic semiconductors because they are considered aspromising materials for field-effect transistors [1], light-emitting diodes [2], chemical sensors [3], and solar cells [4]. Most of materials of this kind are polymers with conjugated aromatic rrings and multiple bonds, which have a delocalized system of π-electrons. The delocalization of electrons is due to the migration of excitons [5], which is of particular interest for chemical sensors and solar cells. In a polymeric sensor material, the diffusion of long-lived excitons along the polymer chain provides a multifold amplification of the analytical signal, which is a desirable positive effect [3]. By contrast, a long exciton lifetime is undesirable in solar cells because of reducing the charge separation efficiency [4].

Thus, it is of interest to reveal factors affecting the lifetime and diffusion length of excitons in organic materials.

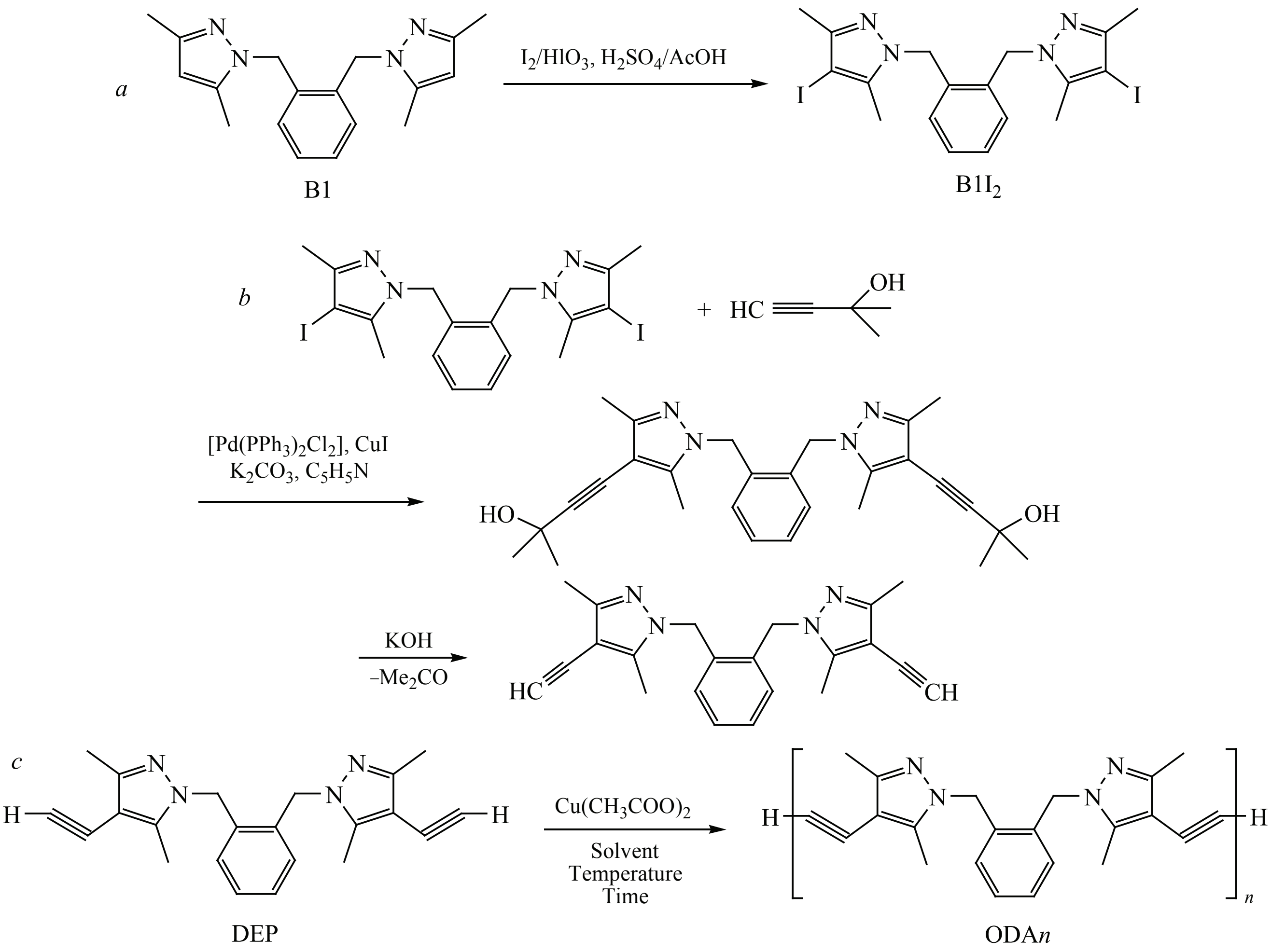
One of factors of this kind is the conjugation length of the system of π-electrons. This length is reduced by introduction into a repeating unit a hexane ring [6], an ether linkage [7, 8] or $CH_2$ group [8]. Polymer materials with broken conjugation of π-electrons are of interest because they can be implemented as self-organizing aggregates in which repeating units are linked to each other by a noncovalent interaction [9]. Materials of this kind are are known as supramolecular. They can find use in optoelectronic devices, and, therefore, are studied now together with the classical polymers in which repeating units are linked by covalent bonds [10].

At present, supramolecular materials are constructed on the basis of conjugated molecules. This approach looks like generally accepted rather than based on fundamental limitations of physicochemical nature. An interesting task in this situation is to study the fluorescence quenching, which depends on the exciton migration, in organic polymers with btoken intramolecular conjugation and aggregation capability. To solve this problem, we used in the present study oligomers based on diacetylene compounds, with a chain length of 2 to 40 repeating units.

## EXPERIMENTAL

**Synthesis of diacetylene oligomers.** The compounds under study were synthesized by the Glaser's reaction [11] by polycondensation of DEP monomer (see scheme, *c*). Divalent copper was used as a catalyst [12], which simplifies the reaction as compared with its conventional version [11]. The general formula of the synthesized

**Scheme.** Synthesis of diacetylene oligomers and their monomer compound



(*a*) Iodination of the ligand, (*b*) synthesis of the monomer, and (*c*) polycondensation of the monomer.

oligomers can be written as ODAn, where n is the chain length. Monomer compound DEP was synthesized in accordance with parts a and b of the scheme from 1,2-bis[-(3,5-dimethylpyrazol-1-yl)dimethyl]benzene (B1) and 2-methyl-3-butyn-2-ol (Favorsky carbinol). The synthesis of the B1 ligand and its ability to form aggregates and also complexes with seven cations were described in [13]. Monomer compound DEP is its diethynyl derivative synthesized by the previously described procedure [14]. All the reagents were purchased from Sigma-Aldrich. The number of repeating units in the oligomer chain was adjusted by choosing the

Reaction conditions for synthesis of diacetylene oligomers with different number of repeating units in the backbone

| Compound | Number of repeating units in the backbone | *T*, °C | τ, min | Solvent | Yield, % |
|---|---|---|---|---|---|
| ODA2 | 2 | 0 | 15 | Pyridine | 85 |
| ODA5 | 5 | 20 | 5 | Diethylamine | 81 |
| ODA12 | 12 | 20 | 15 | » | 98 |
| ODA40 | 40 | 50 | 60 | » | 68 |

reaction temperature and duration. Reaction conditions for synthesis of diacetylene oligomers with the backbone length of 2, 5, 12 and 40 repeating units are listed in the table.

$^1$H NMR spectra of the synthesized compounds were measured with a Bruker 3500 instrument in a $CDCl_3$ solution. For ODA2 oligomer, the spectrum demonstrated the following set of signals δ (ppm): 2.19 s (9H, Pz–$CH_3$), 2.22 s (3H, Pz–$CH_3$), 2.29 s (9H, pZ–$CH_3$), 2.31 s (3H, Pz-$CH_3$), 3.19 s (2H, ≡C), 5.27 s (8H, $CH_2$), 6.72 s (4H, Ph), and 7.21 s (4H, Ph). The mass spectrum of this compound, measured with a Bruker micrOTOF instrument, has a peak with $m/z = 683$, which corresponds to a singly protonated compound with formula $C_{44}H_{42}N_8$. Thus, analysis of the $^1$H NMR spectrum and mass spectrum confirms that the compound we synthesized has the structural formula shown in scheme *c*.

For ODA5, ODA12, and ODA40 oligomers, the $^1$H NMR spectra have no significant difference, except the intensity of the signal of protons from terminal CH groups (3.19 ppm), which decreases as the chain becomes longer. The ratio of the signal area from $CH_2$ groups (5.27 ppm) to the signal area from terminal CH groups (3.19 ppm) is proportional to the number of repeating units in the oligomer chain. It was used to calculate this number. The ratio was 4.2, 9.9, 23.4, and 73.7 for ODA2, ODA5, ODA12, and ODA40 compounds, respectively.

The B1 ligand incorporated into oligomer backbone is expected to retain its features described in [13] for free standing ligand. These are complexation with cation Cu(II) and non-covalent aggregation at the concentration above $10^{-4}$ M. In this case, the copper cation must be a quenching agent for the fluorescence of the oligomer. All the ODAn oligomers are soluble in tetrahydrofuran (THF). This solvent was used in optical absorption and fluorescence measurements of the compounds under study. The molar concentration of all solutions is given per single repeating unit.

**Methods of study.** The most interesting properties of the compounds we synthesized are the efficiency of fluorescence quenching due to the interaction with a quencher and the conjugation length of the π-electrons system. The fluorescence quenching efficiency was evaluated by the parameter $Q$, which is expressed by the equation:

$$Q = I_0/I - 1, \quad (1)$$

where $I_0$ is the initial fluorescence intensity and I that upon interaction with the quenching agent.

This parameter represents a product of Stern–Volmer constant multiplied by quencher concentration of the quenching agent [15]. This way to evaluate the fluorescence quenching efficiency was chosen because the dependence of the ratio between the fluorescence intensities before and after the quenching on the concentration of the quenching agent may be nonlinear as, e.g., that described in [16]. In this case, the Stern–Volmer “constant,” calculated as the derivative of a curvilinear function, becomes dependent on the concentration of the quenching agent and will contain an error of a graphical or numerical differentiation.

The molar concentrations of the quenching agent and of the ligand in the oligomer chain, used in the present study, always had the same absolute value, and, therefore, Eq. (1) makes it possible to exclude from the estimate of the fluorescence quenching efficiency the error associated with the differentiation of a nonlinear Stern–Volmer dependence. The Cu(II) cation selected as the fluorescence quencher was always added as the $CuCl_2$ salt. All fluorescence measurements of the compounds under study were made with a PerkinElmer LS-55 spectrofluorometer.

The conjugation length of the π-electrons system was estimated by the method based on measuring the optical absorption spectrum in the visible and UV spectral ranges [17]. The essential of this method is the fact that optical absorption spectrum undergoes specific changes with increasing of oligomer chain length while the oligomer length does not exceed the conjugation length. When the conjugation length is reached and the oligomer chain is lengthened further, the absorption spectrum ceases to change. All the optical absorption spectra were measured with a Shimadzu UV-2600 spectrophotometer. The size of aggregates into which molecules of the compounds under study may combine was estimated using a Malvern Zetasizer nano dynamic light scattering (DLS) meter.

Properties of diacetylene oligomers. The optical absorption spectra of diacetylene oligomers with 2 and 40 repeating units and of the monomer are shown in Fig. 1. It can be seen that the absorption spectra of both oligomers contain the same, but higher intensity bands as those in the spectrum of the monomer. The characteristic fundamental change of the absorption spectrum, with respect to that of the monomer, observed in [17] with increasing length of the conjugated diacetylene oligomer chain is not observed for the diacetylene oligomers synthesized. The "red" (bathochromic) shift of the absorption bands is also not observed neither for increase in oligomer length from 2 to 40, nor for the transition from monomer to dimer. In other words, the system of π-electrons of each monomer unit is localized in these compounds. This result corresponds to that expected because the pyrazole rings and benzene ring in the B1 ligand are linked by $CH_2$ groups breaking the electron conjugation.

The excitation and emission spectra for the fluorescence of all the compounds ODAn are similar to each other. The maximum of the excitation spectrum lies within the range 370–385 nm. However, we used the excitation wavelength of 400 nm in further measurements of the fluorescence from ODAn compounds. The reason of such a choice is the possibility to decrease the optical density of a solution at the excitation wavelength with acceptable loss of the emission intensity. This is important in working with high concentration solutions whose optical density in the UV spectral range may exceed a value of 2 (Fig. 1).

The fluorescence spectra of ODA40 compound at various concentrations are shown in Fig. 2. Three broad bands with peak intensities of about 420, 445, and 490 nm can be distinguished in these spectra. With increasing concentration, the intensity of the band at 490 nm grows and this bands becomes dominant at a concentration of 9 × $10^{-4}$ M. This behavior indicates that, with increasing solution concentration, aggregates are formed due to the noncovalent interaction upon a decrease in the average distance between molecules to a rather small value.

The aggregation of the compounds under study is confirmed by DLS measurements. Unfortunately, the positions and widths of the DLS peaks on the particle size axis are unstable and give no way of unambiguously relating the aggregate size to the oligomer length. Nevertheless, it can be stated that the size of the aggregates being formed is about 20 nm, and the "tail" of the widest DLS peaks demonstrates the presence of particles up to 300 nm in size.

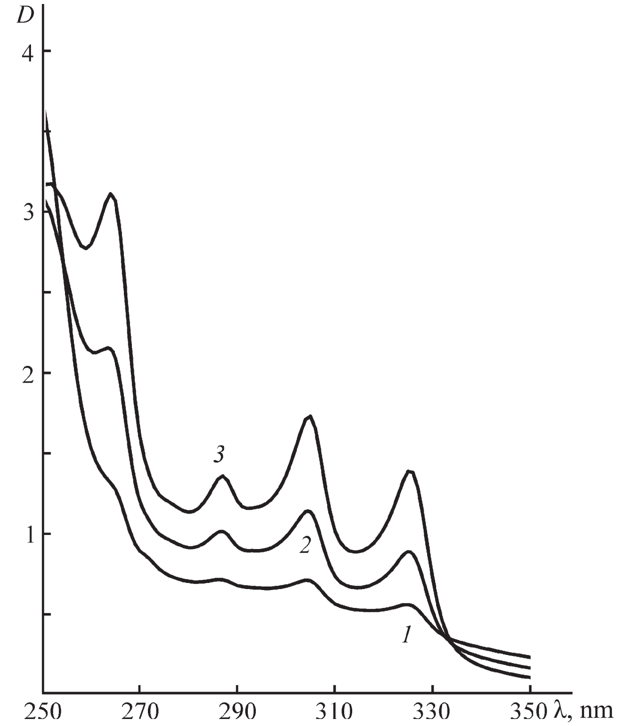


**Fig. 1.** Optical absorption spectra of (*1*) DEP monomer and (*2–3*) diacetylene oligomers (*2*) ODA2 and (*3*) ODA40. Concentration 9 × $10^{-4}$ M. (*D*) Optical density and (λ) wavelength.

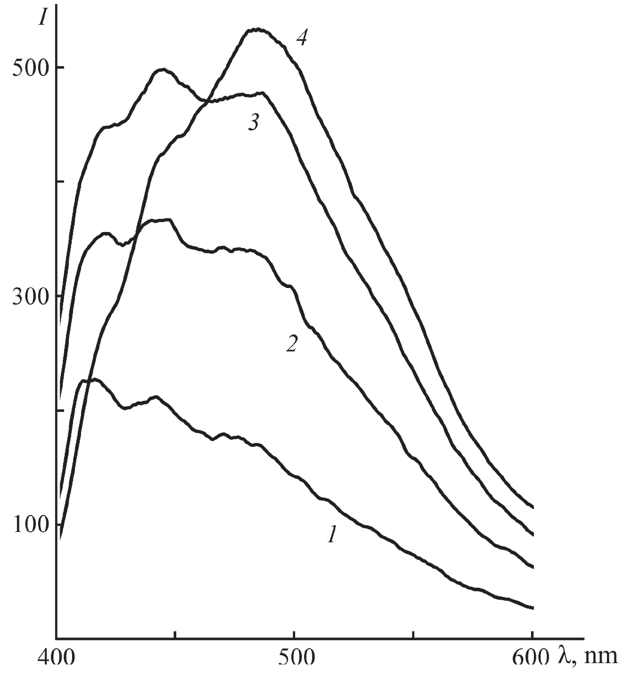


**Fig. 2.** Fluorescence spectra of the diacetylene oligomer ODA40 at various concentrations. Excitation wavelength 390 nm. (*I*) Intensity and (λ) wavelength; the same for Fig. 3. Concentration (M): (*1*) 1.3 × $10^{-4}$, (*2*) 3.8 × $10^{-4}$, (*3*) 6.4 × $10^{-4}$, and (*4*) 9 × $10^{-4}$.

At present, three types of aggregates formed by molecules in the ground (non-excited) state are distinguished. These are aggregates of H and J types [18] and also на joint type aggregates [19]. All of these yield characteristic bands in the absorption spectrum, which can be used to identified the type of an aggregate. A particular type of aggregates is constituted by excimers [20], which are formed only from excited molecules and, therefore, are only seen in the fluorescence spectra and give no contribution to the absorption spectrum.

In our case, we can reliably determine that there are no bands associated with J-type aggregates and those of a joint type in the absorption spectrum. The absence of bands associated with H-type aggregates cannot be considered reliably determined because these bands may lie in the short-wavelength part of the spectrum, which cannot be measured with sufficient accuracy because of the strong absorption by THF. The excimer nature of the band at 490 nm is also consistent with all the available data. Thus, a type-H aggregate or an excimer may be responsible for this band. It is also possible that the excimer is formed from a preliminarily formed H-aggregate.

We further used the emission band at 490 nm to study the efficiency of fluorescence quenching in ODAn compounds by Cu(II) cations. The variation of the intensity of this band upon interaction with an equimolar amount of Cu(II) with respect to the ligand is shown in Fig. 3 for ODA12 oligomer. The copper cation also quenches the emission in the 490-nm band for the rest of the oligomers under study, but the quenching efficiencies calculated by Eq. (1) are different. The dependence of the quenching efficiency on the length of the oligomer chain is shown in Fig. 4. It can be seen that the maximum fluorescence quenching efficiency is reached at an oligomer chain length of 12 repeating units.

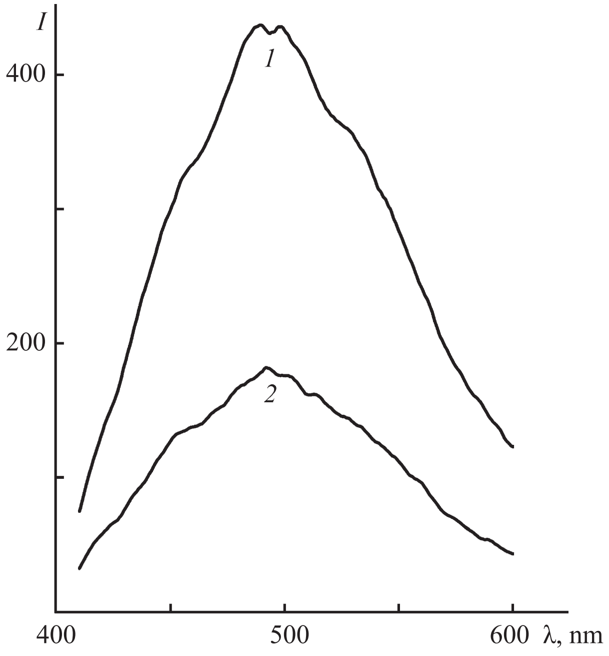


**Fig. 3.** Quenching of the fluorescence of the diacetylene oligomer ODA12 by the Cu(II) cation. (*1*) Initial fluorescence and (*2*) that upon interaction with an equimolar amount of copper chloride.

## RESULTS AND DISCUSSIONS

The unequal quenching efficiencies for oligomers with different chain lengths point to the existence of a collective effect which has an influence on the whole chain. The electron delocalization cannot be the reason for this effect because the electron conjugation lengths of all the compounds studied is equal to single repeating unit. In this situation, there appears a substantiated assumption that the observed collective effect is due to the propagation of delocalized excitons in a supramolecular aggregate.

At present, delocalized excitons have been observed

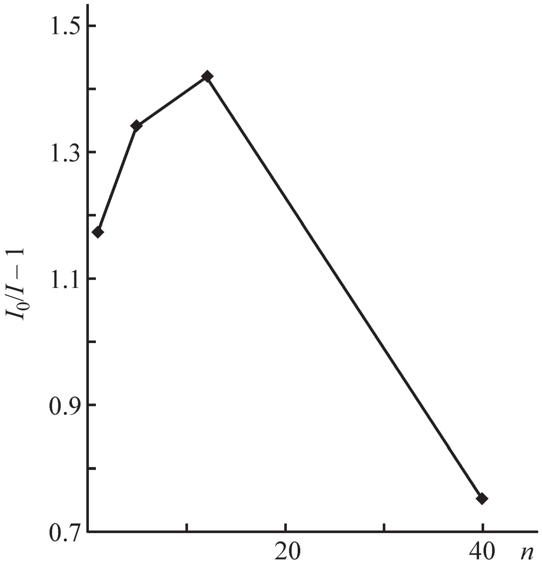


**Fig. 4.** Fluorescence quenching efficiency vs. the length n of the oligomer chain. ($I_0/I$) Ratio between the initial fluorescence intensity and that upon interaction with the quenching agent.

experimentally in noncovalent aggregates [10]. Their propagation length is about 10 repeating units. However, the aggregates studied in [10] were formed from conjugated molecules having no oligomer structure. For this reason, the term “repeating unit” is understood by the authors as a constituent of a supramolecular aggregate, which differs from its meaning in the present study and complicates the comparison of results.

The theory of propagation of a delocalized exciton in a type-H aggregate was considered in [21]. In this study, its motion is compared to rolling of a solid ball over a spring mattress in which each spring is an analog of a molecule in an aggregate. The delocalization of an exciton in this model is due to the resonance interaction of neighboring molecules and is limited by the disorder in their arrangement. If we assume that aggregate with the most regular structure is formed from the oligomer with a chain length of 12, then the highest fluorescence quenching efficiency for this oligomer can be explained in terms of the model [21]. However, the applicability of this model to molecules with btoken conjugation remains questionable because the model has been developed to describe conjugated molecules.

Nevertheless, the propagation of delocalized excitons was also observed in [8] for a polyelectrolyte in which the conjugation was btoken due to the ether linkage between repeating units. According to [8], this effect can be attributed to the helical conformation of the polymer molecule, for which a resonance interaction appears between neighboring coils of the spiral, as it occurs in the H-aggregate.

If we take into account that fluorescence quenching efficiency was enhanced with respect to the repeating by up to a factor of 25 and the excitons were propagated in both direction from the place of their generation, then the exciton delocalization range can be estimated as approximately 12 coils of the molecular spiral [8]. This is in good agreement with the results of the present study and data of [10]. The difference of our results from those obtained in [10, 21] consists in the fact that in our case aggregate is formed from non-conjugated molecules. In compounds P1 and P2 from [8], the conjugation of the polymer chain is btoken, but neither the chain length nor the molecular mass was specified for these compounds, which impairs the informative value of this publication. In addition, the repeating unit of compounds P1 and P2 has a structure different from that in the present study.

Thus, the results we obtained supplement those published previously and confirm the possibility of appearance of a collective effect in a supramolecular aggregate of non-conjugated molecules. The mechanism of a collective effect in the absence of an electron conjugation can be based on the formation of delocalized excitons, in which aggregated oligomer chains are involved [21].

## CONCLUSIONS

(1) The system of π-electrons of each repeating unit of the diacetylene compounds studied is localized and cannot be responsible for the collective effect which has an influence on the whole oligomer chain.

(2) The dependence of the fluorescence quenching efficiency on the number of repeating units in the chain is indicative of the existence of a collective effect operative along the entire oligomer length.

(3) The highest fluorescence quenching efficiency at a chain length of 12 repeating units is consistent with the model in which the collective effect is due to the formation of delocalized excitons in a noncovalent supramolecular aggregate.

(4) The results obtained in the study indicate that supramolecular materials for electronic devices can be constructed from non-conjugated molecules, which extends the variety of materials suitable for this purpose due to the use of chemical compounds not previously considered as such.

## ACKNOWLEDGMENTS

This work was supported by grant 12.37.128.2011 for basic research according to the Program of advancement of St. Petersburg State University.

Some equipment of the "Center for chemical analysis of materials" at St. Petersburg State University was used in this research.

The useful assistance of S.S. Levichev is greatly appreciated by authors.

## REFERENCES

1. Nielsen, C.B. and McCulloch, I., Progr. Polym. Sci.; 2013, http://dx.doi.org/10.1016/j.progpolymsci. 2013.05.003.
2. Chen, J.-T. and Hsu, C.-S., Polymer 2013; http://dx.doi.org/10.1016/j.polymer.2013.04.037.

3. Andrew, T.L. and Swager, T.M., *J. Polym. Sci. B: Polym. Phys*., 2011, vol. 49, pp. 476–498.
4. Grancini, G., Maiuri, M., Fazzi, D., et al., *Nature Mater*., 2013, vol. 12, pp. 29–33.
5. Kose, M.E., Graf, P., Kopidakis, N., et al., *ChemPhysChem*., 2009, vol. 10, pp. 3285–3294.
6. Clavaguera, S., Dautel, O.J., Hairault, L., et al., *J. Polym. Sci.: A: Polym. Chem*., 2009, vol. 47, pp. 4141–4149.
7. Chasteena, S.V., Carter, S.A., and Rumbles, G., *J. Chem. Phys*., 2006, vol. 124, pp. 214704-1–214704-6.
8. Xie, D., Parthasarathy, A., and Schanze, K.S., *Langmuir,* 2011, vol. 27, pp. 11732–11736.
9. Prokhorov, V.V., Pozin, S.I., Lypenko, D.A., et al., *Chem. Phys. Lett*., 2012, vol. 535, pp. 94–99.
10. Lim, J.M., Kim, P., Yoon, M.-C., et al., *Chem. Sci*., 2013, vol. 4, pp. 388–397.
11. Siemsen, P., Livingston, R.C., and Diederich, F., *Angewandte Chem*., *Int. Ed*., 2000, vol. 39, pp. 2632–2657.
12. Balaraman, K. and Kesavan, V., *Synthesis*, 2010, vol. 20, pp. 3461–3466.
13. Vlasov, Yu.G., Levichev, S.S., and Kruchinin, A.A., *Russ. J. Appl. Chem.,* 2012, vol. 85, no. 6, pp. 940-944.
14. Potapov, A.S., Khlebnikov, A.I., and Vasilevskii, S.F., *Russ. J. Org. Chem.,* 2006, vol. 42, no. 9, pp. 1368-1373.
15. Lakowicz, J.R., *Principles of Fluorescence Spectroscopy*, New York, 1999, p. 239.
16. Banjoko, V., Xu, Y., Mintz, E., and Pang, Y., *Polymer*, 2009, vol. 50, pp. 2001–2009.
17. Pilzak, G.S., Baggerman, J., van Lagen, B., et al., *Chem. Eur. J*., 2009, vol. 15, pp. 2296–2304.
18. Yao, H., Domoto, K., Isohashi, T., and Kimura, K., *Langmuir*, 2005, vol. 21, pp. 1067–1073.
19. Kirkus, M., Wang, L., Mothy, S., et al., *J. Phys. Chem. A*, 2012, vol. 116, pp. 7927–7936.
20. Wanichacheva, N., Prapawattanapol, N., Lee, V.S., et al., *J. Luminescence*, 2013, vol. 134, pp. 686–690.
21. Spano, F.C., *Accounts Chem. Research*, 2010, vol. 43, pp. 429–439.