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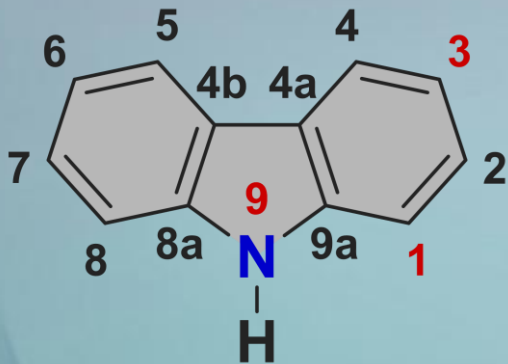
REAKTIVNI INTERMEDIJERI U FOTOLIZI KARBAZOLA

KEMIJSKI SEMINAR 1
Doktorski studij: Kemija (smjer: Organska kemija)

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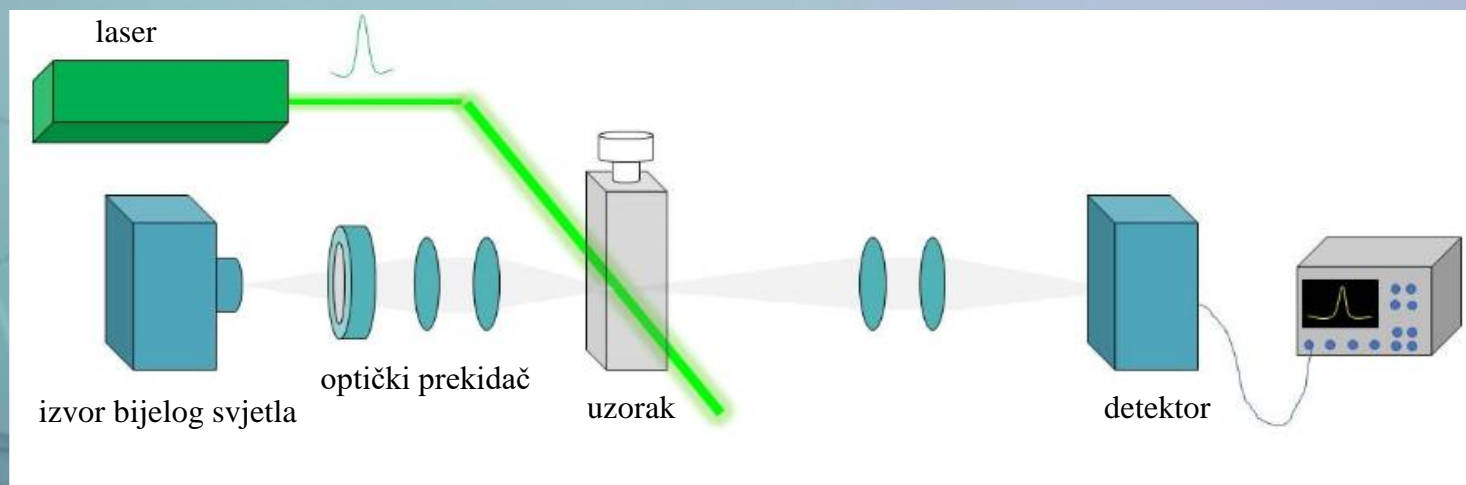
DERIVATI KARBAZOLA



- jaka apsorpcija u UV području, visoki kvantni prinos fluorescencije i visoka energija tripletnog pobuđenog stanja
- primjena u OLED-ima, organskim solarnim ćelijama, fotokatalizi, kao biološki aktivni spojevi
- UV zračenje → fotofizički i fotokemijski procesi → reaktivni intermedijeri

LASERSKA PULSNA FOTOLIZA (LFP) I TRANZIJENTNA APSORPCIJSKA SPEKTROSKOPIJA (TA)

- pulsna fotoliza – intenzivni bljesak vidljive ili ultraljubičaste svjetlosti
- laserska pulsna fotoliza – kratki laserski pulsevi, *pump-probe* tehnika
- LFP → specifičan slučaj TA
- TA – obuhvaća sve *pump-probe* tehnike kojima se ispituju kratkoživaća pobuđena stanja mjerenjem promjene apsorbancije na kratkim vremenskim skalama



S. R. Salman, Chemical Reactions Studied by Electronic Spectroscopy, u Encyclopedia of Spectroscopy and Spectrometry, Elsevier, 1999, str. 216–222.

<https://uml.chemistry.unimelb.edu.au/research-2/technique-descriptions/nanosecond-gated-spectroscopy/laser-flash-photolysis/>

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CILJ I MOTIVACIJA ISTRAŽIVANJA

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Article

Laser Flash Photolysis of Carbazole in Solution: Cation Radical as a Source of Carbazolyl Radical

Malgorzata Bayda-Smykaj,* Gotard Burdzinski, Jacek Koput, Magdalena Grzelak, Gordon L. Hug, and Bronislaw Marciniak

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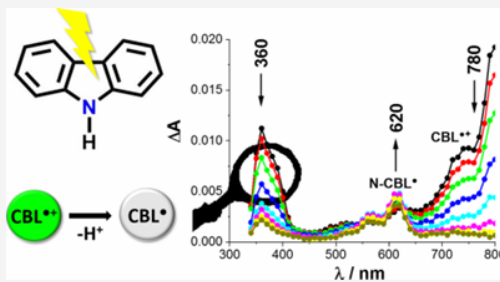
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ABSTRACT: In the course of 266 nm nanosecond laser flash photolysis of carbazole (CBL) in acetonitrile, we discovered a new transient absorption band centered at 360 nm that has been heretofore unreported despite numerous reports on similar topics. To put some limits on possible transients responsible for this absorption band and thus to solve the mechanism of CBL photolysis, we employed the strategy of selectively blocking the CBL active sites by various modifications in the structure. This strategy was supported by the use of the solvent effect and triplet quenching by molecular oxygen. As a result, the mechanism of carbazole photolysis has been elucidated, part of which was our new discovery that the carbazolyl radical can be formed by the deprotonation of the cation radical. The proposed mechanism has been supported by the reaction with TEMPO, theoretical calculations, and also LC-MS/UV analysis of the stable photoproducts. Given the high impact of CBL-based compounds as one of the key compounds in material science (e.g., OLEDs, TADF, and other light-emitting materials), the understanding of the observed radical-driven processes that occur in the photolysis of carbazole seems to be of great interest.



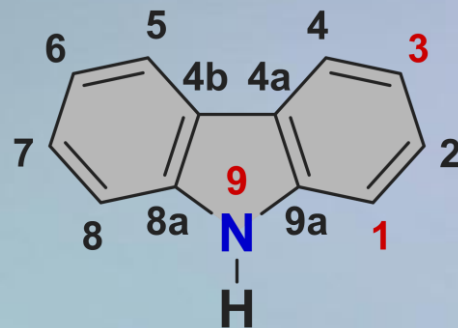
- u radu je proučavana fotoliza karbazola u acetonitrilu primjenom nanosekundne laserske pulsne fotolize pri 266 nm
- otkrivena je nova tranzijentna vrpca oko 360 nm koja prije nije bila zabilježena
- tranzijentna vrpca – spektralni „potpis”

M. Bayda-Smykaj, G. Burdzinski, J. Koput, M. Grzelak, G. L. Hug, B. Marciniak, *J. Phys. Chem. B* 129 (2025) 1614–1625.

F. Dickinson, Chapter 3: TA Transient Absorption, u *Advanced Spectroscopic Techniques*, 2021, str. 31–39.

S.-Y. Kim, Y.-J. Cho, A.-R. Lee, H.-j. Son, W.-S. Han, D. W. Cho, S. O. Kang, *Phys. Chem. Chem. Phys.* 19 (2017) 426–435.

PRIJAŠNJA SAZNANJA O INTERMEDIJERIMA KARBAZOLA



<i>Apsorpcijski maksimum / nm</i>	<i>Predloženi intermedijer</i>
~420	$^3\text{CBL}^*$
~550	$\text{CBL}^{\bullet+}$
~600	$\text{CBL}^{\bullet+}$
~620	$^1\text{CBL}^*$
~780	CBL^{\bullet}

EKSPERIMENTALNI PRISTUP I NAMJERNO „BLOKIRANJE“ REAKTIVNIH MJESTA

- ns LFP pri 266 nm → Nd:YAG (engl. *Neodymium-doped Yttrium Aluminum Garnet*) laser i ksenonova lampa
- kratki, intenzivni laserski puls pobuđuje otopinu karbazola ili njegovih derivata → vremenski ovisne promjene tranzijentne apsorbancije → vrijeme života i tranzijentni apsorpcijski spektar pojedinih međuprodukata
- uzorci karbazola i derivata pripremaju se u acetonitrilu i cikloheksanu → otopine se propuhuju argonom



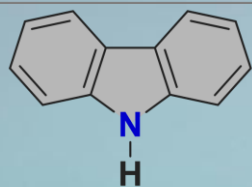
M. Ludwiczak, M. Majchrzak, M. Bayda, B. Marciniak, M. Kubicki, B. Marciniak, J. Organomet. Chem. 750 (2014) 150–161.

M. Bayda-Smykaj, G. Burdzinski, J. Koput, M. Grzelak, G. L. Hug, B. Marciniak, J. Phys. Chem. B 129 (2025) 1614–1625.

G. Burdzinski, M. Bayda, G. L. Hug, M. Majchrzak, B. Marciniak, B. Marciniak, J. Lumin. 131 (2011) 577.

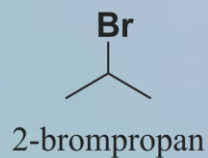
EKSPERIMENTALNI PRISTUP I NAMJERNO „BLOKIRANJE“ REAKTIVNIH MJESTA

Reaktant 1



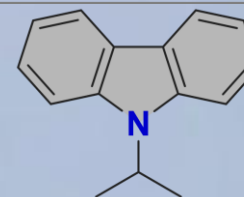
CBL(1)

Reaktant 2

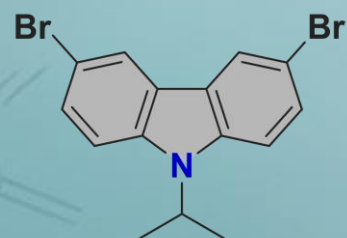


2-bromopropan

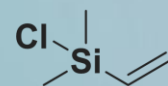
Produkt



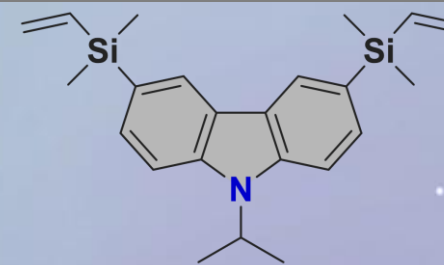
CBL(2)



3,6-dibrom-9-izopropil-9H-karbazol



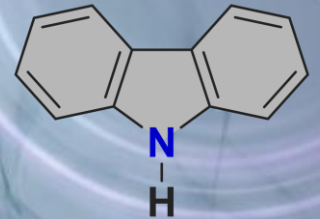
klor(dimetil)vinilsilan



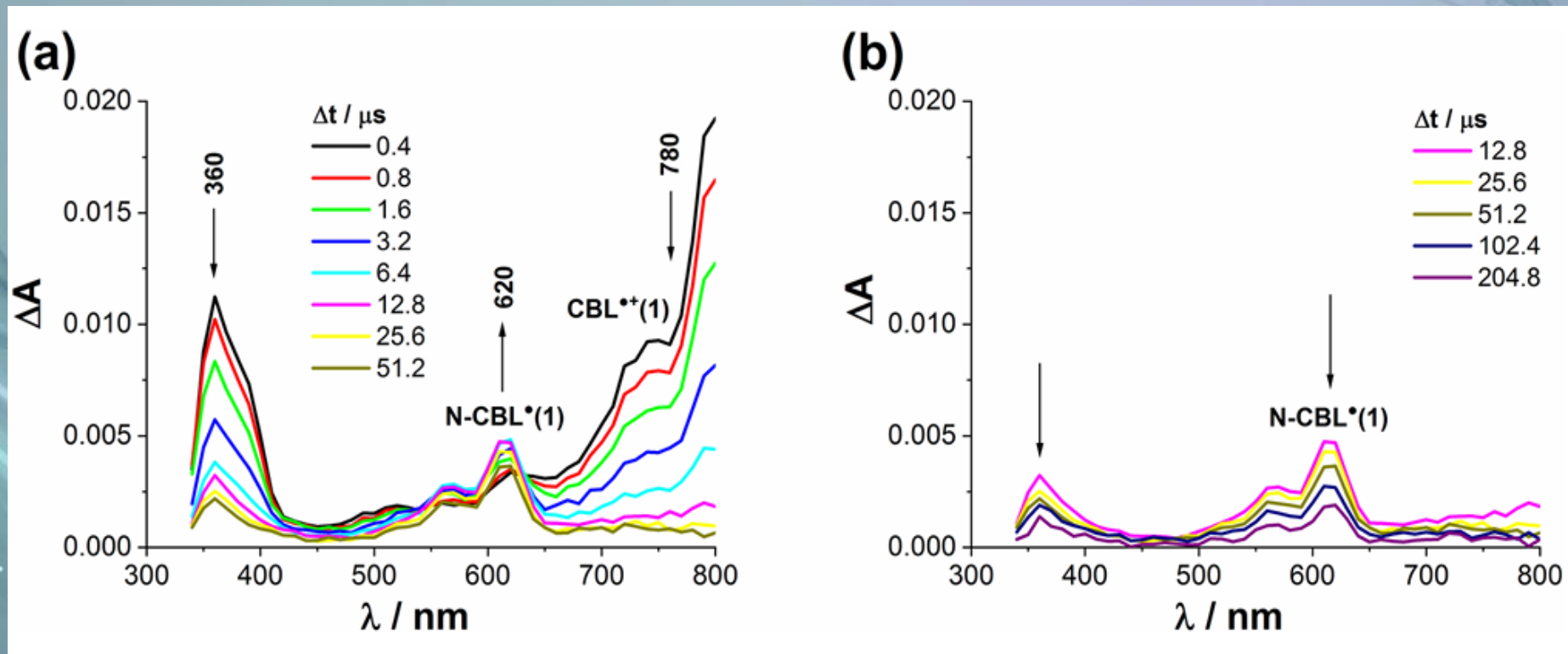
CBL(3)

NOVA TRANZIJENTNA VRPICA I NJEZINA ASIGNACIJA

- intenzivna apsorpcijska vrpca s maksimumom oko 360 nm → problem: jednoznačna asignacija

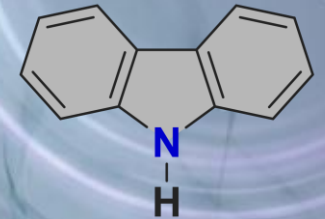


CBL(1)

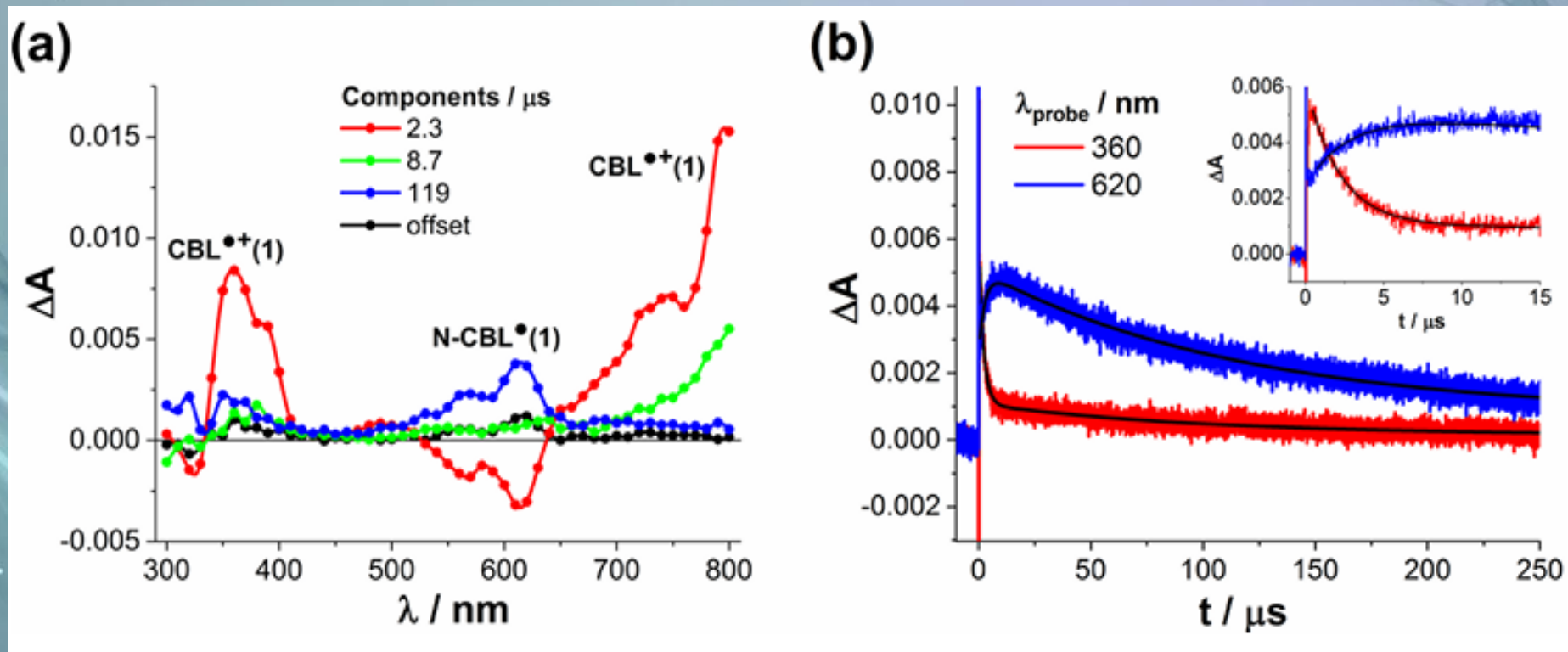


NOVA TRANZIJENTNA VRPICA I NJEZINA ASIGNACIJA

- detaljnija analiza → DAS (engl. *Decay Associated Spectra*) spektri

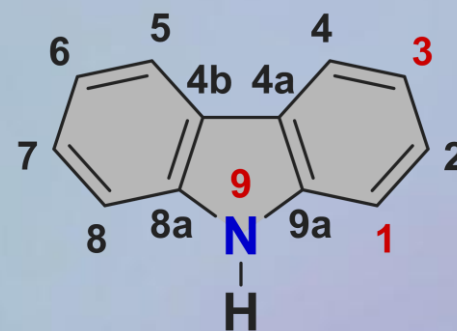


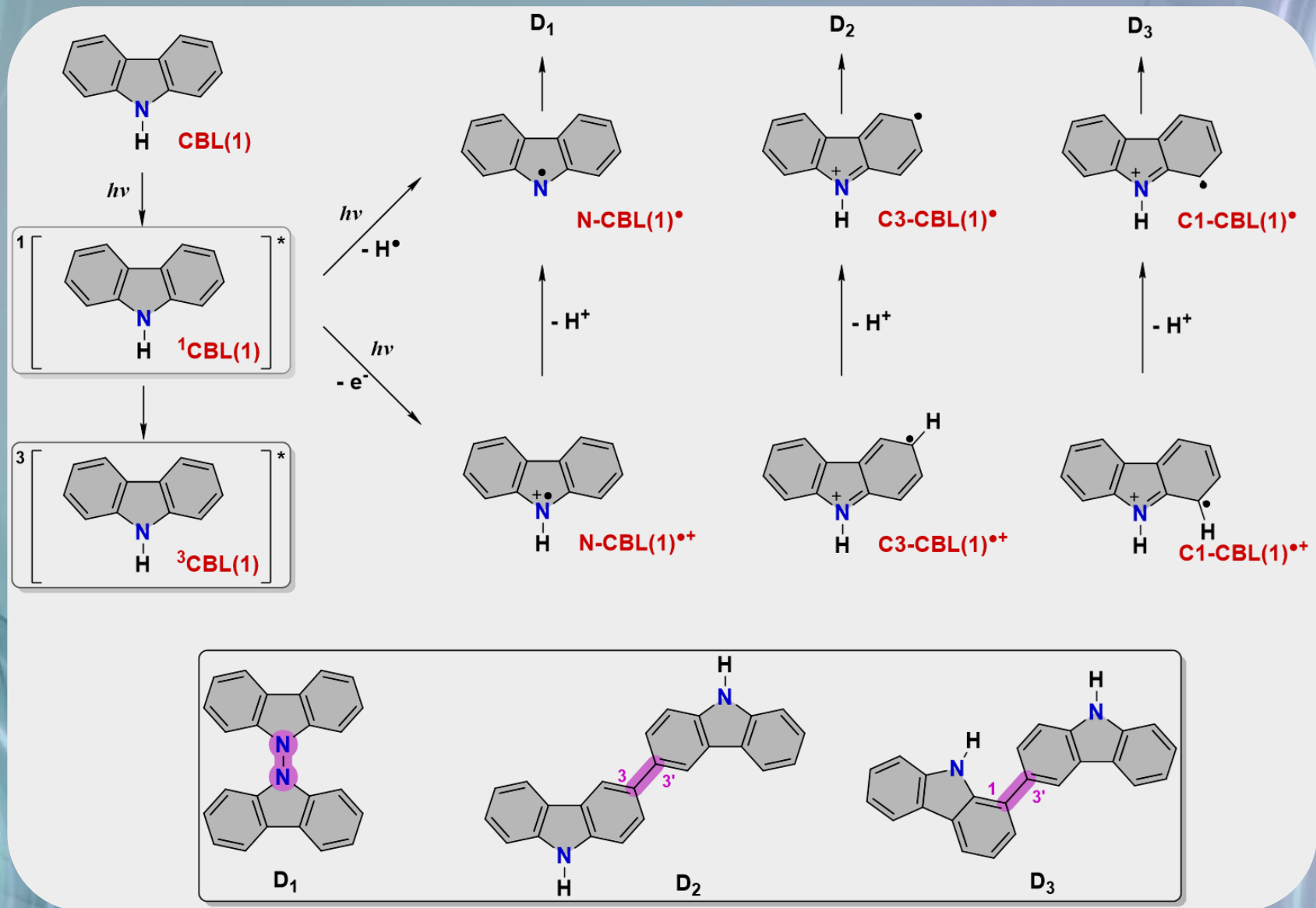
CBL(1)



MEHANIZAM – OD RADIKAL-KATIONA DO KARBAZOLIL-RADIKALA I DIMERA

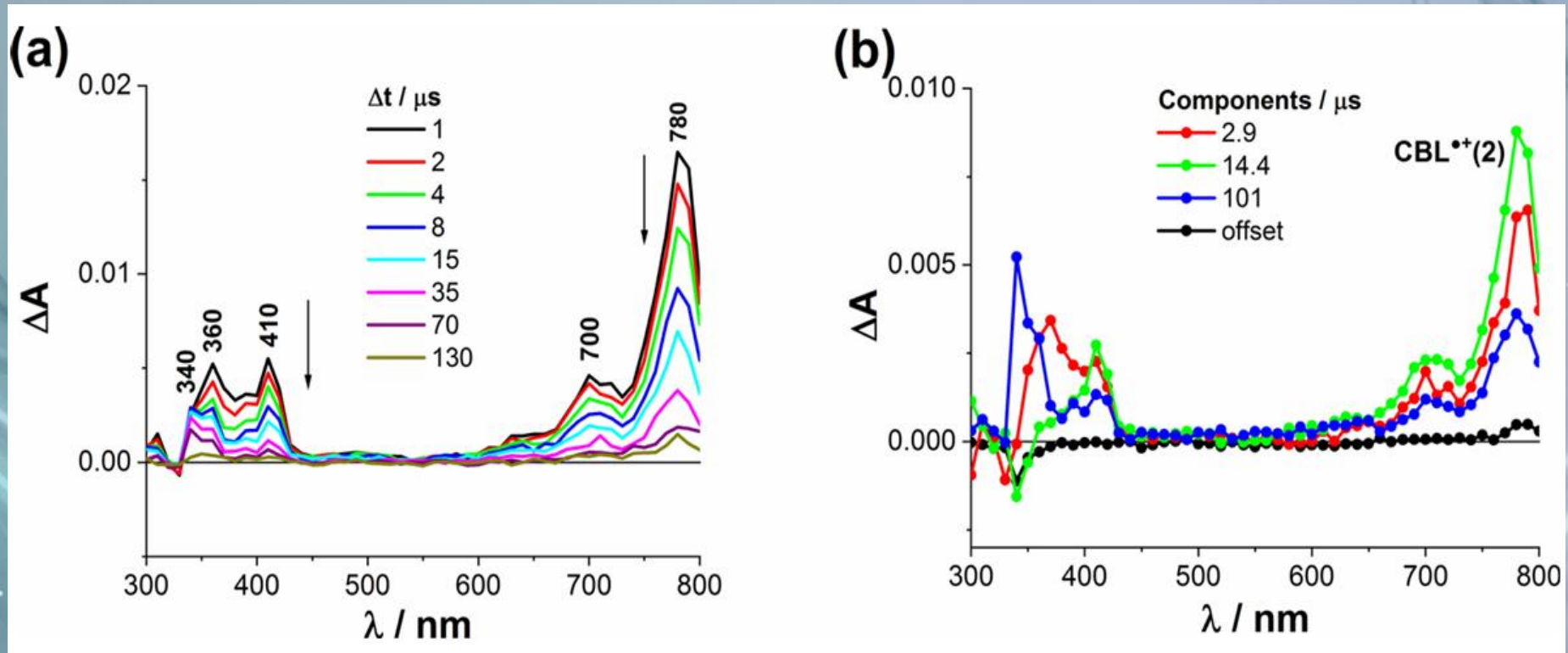
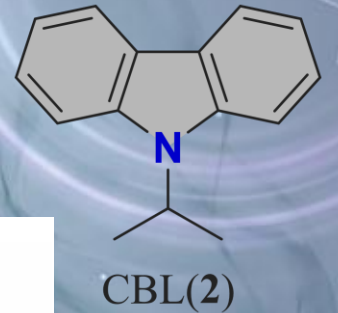
- 1) Pobuda karbazola
- 2) Stvaranje radikal-kationa karbazola
- 3) Pretvorba u karbazolil-radikal
- 4) Nastanak dimera i drugih stabilnijih produkata





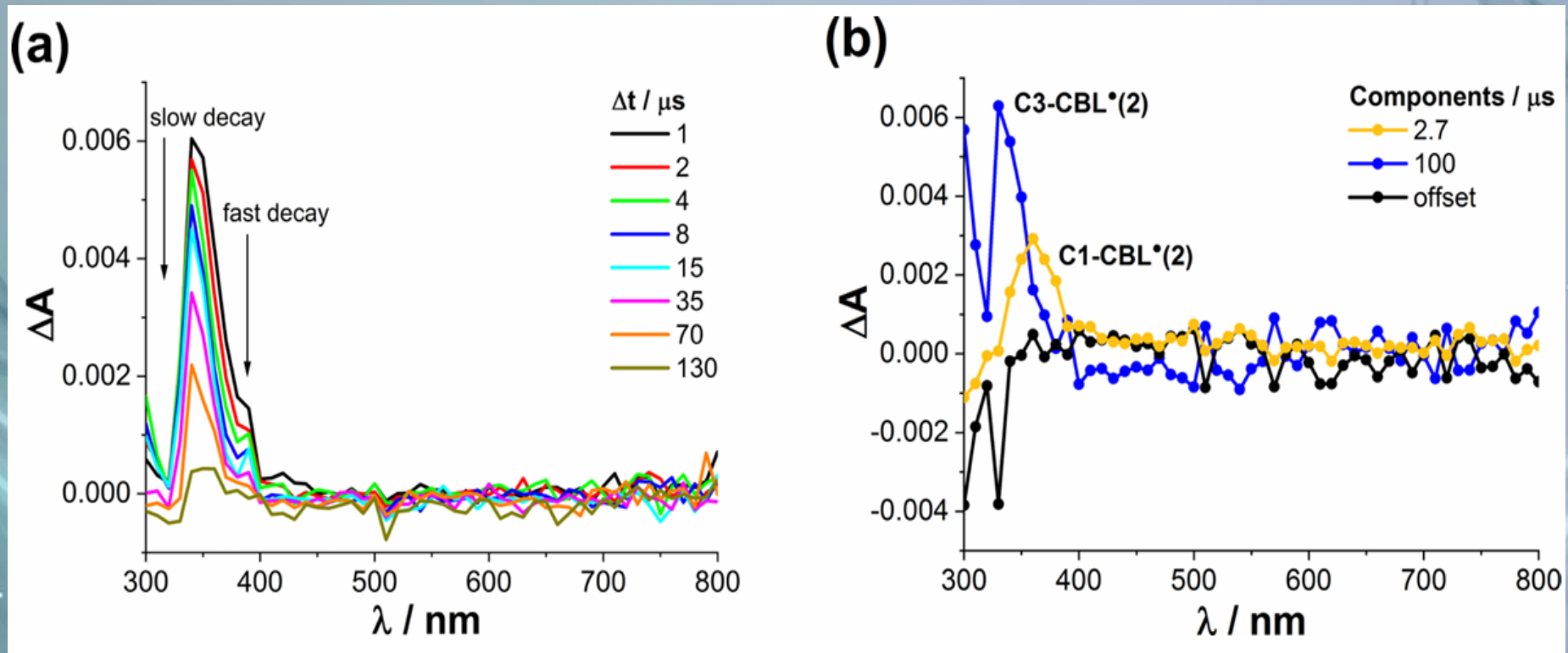
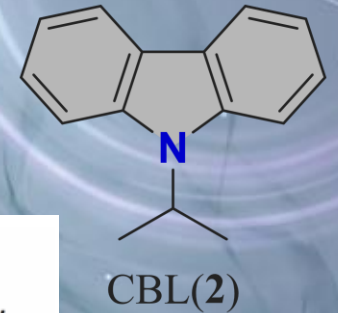
ASIGNACIJA SPEKTRALNIH VRPCEI

- CBL(2) karbazol → supstituiran alkilnom skupinom na dušiku



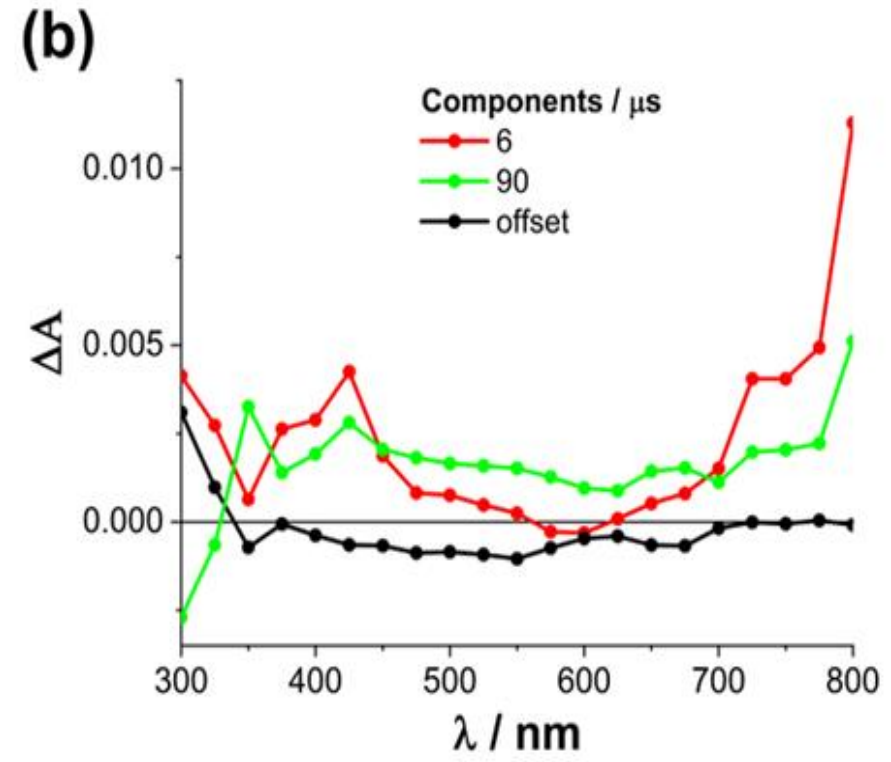
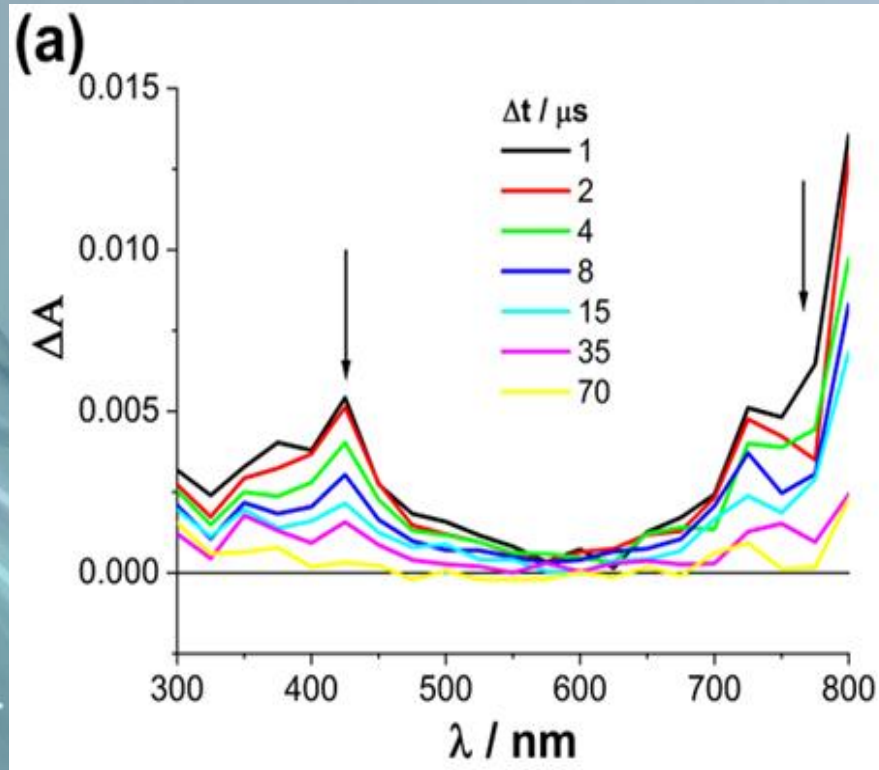
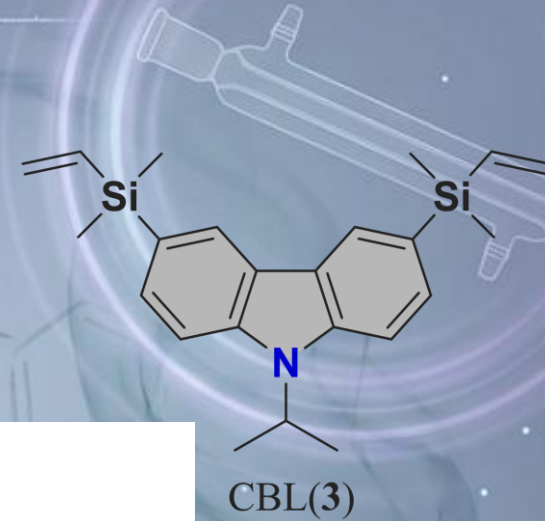
ASIGNACIJA SPEKTRALNIH VRPCEI

- otopina CBL(2) u cikloheksanu



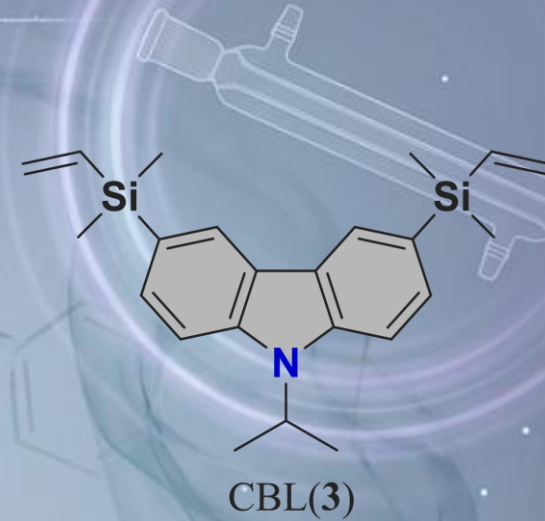
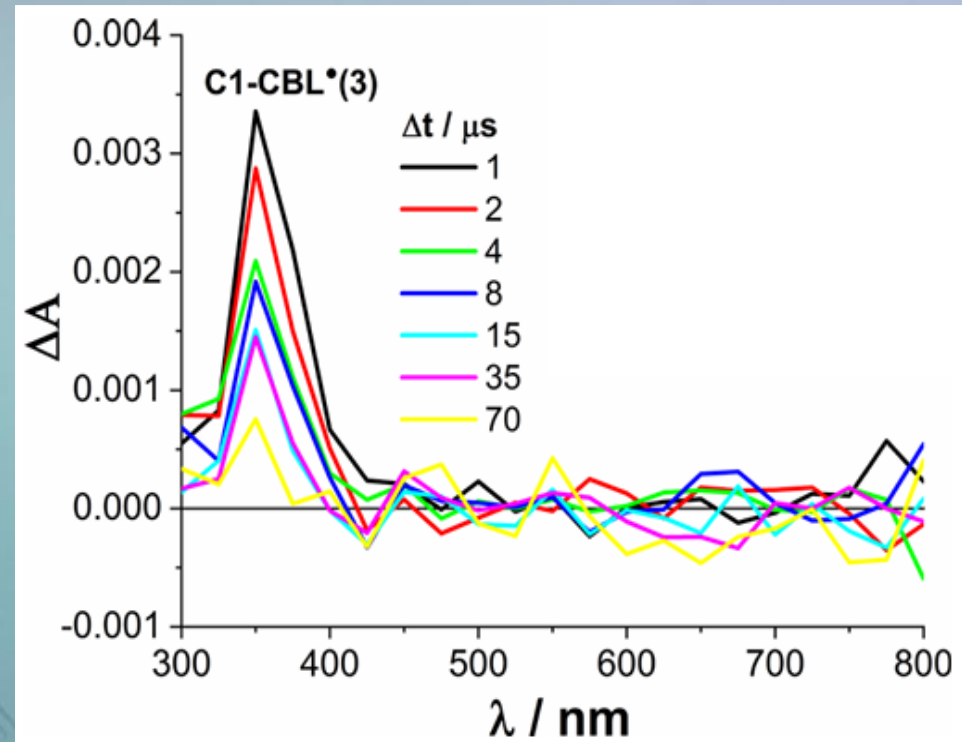
ASIGNACIJA SPEKTRALNIH VRPCEI

- CBL(3) karbazol → favorizira nastanak radikala lokaliziranog na ugljiku na položaju 1



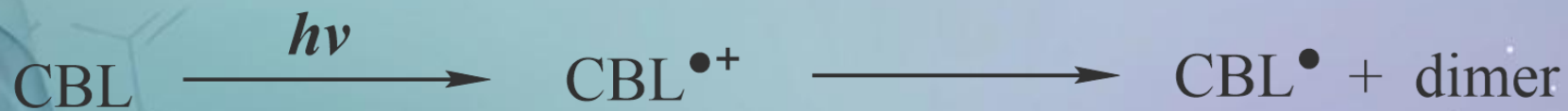
ASIGNACIJA SPEKTRALNIH VRPCEI

- otopina CBL(3) u cikloheksanu



ZAKLJUČAK

- nova vrpca oko 360 nm → radikal-kation karbazola
- derivati CBL(2) i CBL(3) → spriječen nastanak radikala lokaliziranog na dušiku, favoriziran nastanak radikala lokaliziranih na ugljiku
- svojstva otapala utječu na relativne udjele i vidljivost pojedinih intermedijera → polarni acetonitril favorizira radikal-katione, a nepolarni cikloheksan pogoduje neutralnim radikalima
- radikal-kation, homolitičko cijepanje N–H veze i procesi koji vode dimerizaciji međusobno konkuriraju u stvaranju neutralnih radikala



Hvala na pažnji!