

Spectroscopic and photochemical properties of lycopene, β -carotene, bixin, norbixin and their radical intermediates

By

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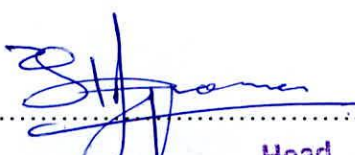
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To my loving son Janitha

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LIST OF ABBREVIATIONS

ACOA	8'-apo- β -carotene-8'-oic acid
AM1	Austin Model 1
Apocar	Apo-carotenoids
ATR-IR	Attenuated Total Reflectance Infra-Red
B3LYP	Becke3-Lee-Yang-Parr
BC	Beta-carotene
Bix	Bixin
BSA	Bovine serum albumin
Car ^{•+}	Carotenoid radical cation
Car	Carotenoids
DFT	Density Function Theory
DSSC	Dye Sensitized Solar Cells
E _g	Band gap energy
Flu	Fluorescence
FTIR	Fourier Transform Infra-Red
HB	Hypocrellin B
HF	Hartree-Fock
HOMO	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
INDO	Intermediate Neglect of Differential Overlap
ITO	Indium tin oxide
LUMO	Lowest unoccupied molecular orbital

Lyco	Lycopene
NB	Norbixin
NPs	Nanoparticles
ORNL	Oak Ridge National Laboratory
PDA	Photodiode array
PET	Photo-induced electron transfer
PTFE	Polytetrafluoroethylene
PV	Photovoltaics
QS	Quinine sulfate
QY	Quantum yield
R _g	Radius of gyration
RHF	Restricted Hartree-Fock method
ROS	Reactive oxygen species
SANS	Small angle neutron scattering
SAS	Small angle scattering
SAXS	Small angle X-ray scattering
SLD	Scattering length densities
TBAPC	Tertiary butyl ammonium perchlorate
TEA	Triethylamine
TLE	Thin Layer Electrolysis
UHF	Unrestricted Hartree-Fock method
UV-vis	UV-visible
UV-vis DR	UV-visible diffuse reflectance
λ_{max}	Maximum absorption wavelength

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Spectroscopic and photochemical properties of lycopene, β -carotene, bixin, norbixin and their radical intermediates

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ABSTRACT

The spectroscopic and photochemical properties of carotenoids, namely, lycopene, β -carotene, bixin, norbixin and their oxidized intermediates were investigated using UV-vis, fluorescence and UV-vis diffuse reflectance spectroscopic (UV-vis DRS) techniques and small angle neutron scattering (SANS) studies. Carotenoids were extracted, purified and isolated from naturally occurring plant materials, all except β -carotene, which was obtained as a standard material. The characterization of isolated molecules was carried out by UV-vis, Fourier Transform Infra-Red (FTIR) spectroscopy and high performance liquid chromatography (HPLC).

The characteristic strongly allowed $S_0 \rightarrow S_2$ electronic transition which comprised of vibronic structures corresponding to the 0-2, 0-1 and 0-0 transitions was observed for all carotenoids in the visible region. Moreover, the fluorescence data revealed a dominant $S_2 \rightarrow S_0$ ($1^1B_u \rightarrow 1^1A_g$) emission at 550 nm for all carotenoids. Radical cations, dications and oxidized intermediate species of carotenoids were generated in CH_2Cl_2 solutions *via* chemical oxidation using anhydrous $FeCl_3$. The nature of intermediate species generated during the chemical oxidation process and subsequent degradation were also studied. The intense emission of the neutral carotenoid molecules when excited at 350 nm was blue shifted during the oxidation process. Oxidized β -carotene, lycopene and norbixin exhibited intense fluorescence peaks at 492, 493 and 500 nm, respectively. These peaks were assigned to intermediate peroxy/epoxy compounds of the three molecules formed with molecular oxygen before the formation of oxidized short-chain stable compounds.

Photodegradation studies of carotenoids demonstrated that the rate of photodegradation was greatly affected by the polarity of the solvent. Lycopene photodegradation in acetone/water mixtures have shown that the photoinduced degradation rate of lycopene is highest in acetone and lowest in a 5% water/acetone mixture. The degradation mechanism changes from first order to second order kinetics as water is introduced to the system. The photochemical stability of carotenoids containing terminal carboxylic groups, bixin and norbixin, chemisorbed onto the surface of TiO₂ semiconductor was also studied. The photodegradation of bixin and norbixin both showed similar but higher rates, compared to the decomposition rates in the absence of the TiO₂ surface. This suggests that both bixin and norbixin have similar decaying pathways, and possibly with a one surface binding site. The interaction between TiO₂ Nps and bixin as well as norbixin was also studied by fluorescence spectroscopy. Fluorescence data revealed that the presence of a single binding site for both carotenoids and their binding constants (K_a) are $2.63 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ and $1.57 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ for bixin and norbixin respectively at 293 K. SANS studies were performed to understand the conformation and self-assembly behavior of bixin and norbixin in *d*-acetone. SANS patterns of bixin and norbixin obtained at three concentrations in acetone demonstrated that the data at all q values best fitted to a FuzzySphere model which explains the scattering from a spherical particle with a fuzzy interface. A computational investigation with an *ab-initio* RHF or UHF/ 3-21G level of theory for the geometrical optimization followed by an *ab-initio* calculation of selected isomers of lycopene were shown that 5-*cis* isomer is more stable than all the other isomer. The data obtained for RHF/6-31G geometrical optimization followed by TD/B3lyp/6-31G excitation energy calculations provided reliable predictions for the excitation energies of neutral carotenoids.